Intellectual Exchange and Innovation Conference on Engineering & Sciences (IEICES)

15 October, 2015

Kyushu University, Fukuoka, Japan

CONFERENCE PROGRAM AND PROCEEDINGS
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Welcome to IEICES!

On behalf of the IEICES 2015 organizing committee, it is my great pleasure to welcome you to the Intellectual Exchange and Innovation Conference on Engineering & Sciences (IEICES), which is being held on 15th October, 2015 at Kyushu University, Japan. The conference brings together academics, researchers and students to share the latest developments and research in the fields of materials, energy and environmental engineering & sciences. The organizing committee has developed an exciting program to give participants an opportunity to present their academic works, concepts and new discoveries. Moreover, participants will have a chance to get to know one another closely.

Before I close, I would like to thank each of your for participating our conference and bringing your expertise to our gathering.

Osama Eljamal
IEICES Chairman
## COMMITTEES

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Prof. Akira Harata

**Conference Chairman**  
Associate Prof. Osama Eljamal

**Conference Coordinator**  
Ahmad Syahrin Idris

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- Qi Shi-Chao
- Ruan Hongcheng
- Tarek Naem Dief
- Wang Zhengxing
- Zhang Lu
## Technical Program

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INVITED SPEAKERS

➢ Prof. Kazuo Arakawa
Professor / Renewable Energy Center, Research Institute for Applied Mechanics, Kyushu University

Biography
- 2001-present: Associate professor at Research Institute for Applied Mechanics RIAM, Kyushu University

University
- 1988-1989: Visiting researcher, University of Washington, USA.
- 1982: Research Associate, RIAM, Kyushu University
- 1982: D.Eng. from Osaka University

Membership in Academic Society
- The Japanese Society for Experimental Mechanics (JSEM)
- The Society of Materials Science, Japan
- The Japan Society for Composite Materials
- The Japanese Society for Non-Destructive Inspection
- The Japan Society of Mechanical Engineers
- Society for Experimental Mechanics

Presentation title
Effect of time derivative of contact area on dynamic friction

Presentation Abstract:
This study investigated dynamic friction during oblique impact of a golf ball by evaluating the ball's angular velocity, contact force, and the contact area between the ball and target. The effect of the contact area on the angular velocities was evaluated, and the results indicated that the contact area plays an important role in dynamic friction. In this study, the dynamic friction force F was given by F= \( \mu N + \eta \frac{dA}{dt} \), where \( \mu \) is the coefficient of friction, N is the contact force, \( \frac{dA}{dt} \) is the time derivative of the contact area A, and \( \eta \) is a coefficient associated with the contact area.

➢ Prof. Shigeo Yoshida
Professor / Renewable Energy Center, Research Institute for Applied Mechanics, Kyushu University

Biography
- Working at Kyushu University since 2013, as a professor in Research Institute for Applied Mechanics

University
- Received B.E. Degree in Engineering Faculty of Kyoto University in 1990

Industry
- Worked in Fuji Heavy Industries (SUBARU) since 1990, as an aerodynamic engineer for aircrafts and wind turbines and transferred to Hitachi in 2012.
- Member of JSME, JSFM, JSES (Director 2008-2010), JWEA (Director 2010-), TSJ and a registered expert of IEC.
- Best Technology Award (JSES, 2007)
- Best Paper Award (JSES 2007, JWEA 2009)
- Best Poster Award (Renewable Energy 2006)

Research
- Fundamental design, aerodynamics, control and safety of wind turbines
- Wind farm performance, fatigue mitigation, layout optimization
- Downwind rotor and tower shadow model
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CFRP ADHESIVE JOINTS AND STRUCTURES FOR OFFSHORE WIND-LENS TURBINE

M R Abusrea1, Shi Yi Jiang1, Dingding Chen2, and Kazuo Arakawa1.
1 Interdisciplinary Graduate School of Engineering Science, Kyushu University, Fukuoka, Japan (mahmoud.r.abusrea.127@s.kyushu-us.ac.jp)
2 National University of Defense Technology, China,
3 Research Institute for Applied Mechanics, Kyushu University, Fukuoka, Japan

Abstract: Novel wind-lens turbine designs can augment power output. Vacuum-assisted resin transfer molding (VARTM) is used to form large and complex structures from a carbon fiber reinforced polymer (CFRP) composite. Typically, wind-lens turbine structures are fabricated in segments, and then bonded to form the final structure. This paper introduces five new adhesive joints, divided into two groups: one is constructed between dry carbon and CFRP fabrics, and the other is constructed with two dry carbon fibers. All joints and CFRP fabrics were made in our laboratory using VARTM manufacturing techniques. Specimens were prepared for tensile testing to measure joint performance. The results showed that the second group of joints achieved a higher tensile strength than the first group. On the other hand, the tensile fracture behavior of the two groups showed the same pattern of crack originating near the joint ends followed by crack propagation.

1. Introduction
Composite materials have high stiffness-to-weight and strength-to-weight ratios, and have been used for many applications including aerospace, automotive, and wind turbine structures [1]. The wind-lens, a curved ring around the turbine blades, is manufactured from six identical parts joined together to form the final structure. Consequently, its performance depends not only on material properties but also on the joining technique. Bonded joints have mechanical advantages over bolted joints because fibers are not cut, and stresses are transmitted more homogeneously [2].

This paper introduces various adhesive bonded joints, made of carbon fiber reinforced polymer (CFRP), for use in offshore wind-lens structures. The main objective of this work was to develop high-strength joint applicable to offshore wind-lens structures. The strengths of five joints were assessed. All joints and CFRP material tested in this study were made using a technique developed from the vacuum-assisted resin transfer molding (VARTM) process.

2. Experimental work
The composite material was CFRP, consisting of a carbon fabric (TENAX STS; 504 g m–2) hardened with a resin (XNR6815/XNH6815). Four unidirectional carbon fabric sheets were stacked and molded together to form plates with an average thickness of 2 mm [1]. All CFRP fabrics were produced using VARTM, a variation of resin transfer molding (RTM) in which a solid mold with a flexible tape-sealed vacuum bag is used to replace the closed mold. In the VARTM process, reinforcements are stacked on a solid mold, which is treated with mold releasing agent and covered with a peel ply and distribution medium. They are enclosed together with an inlet and a vent in a vacuum bag and sealed with gum tape (see Fig. 1).

Joint strengths were evaluated via tensile testing using standardized test specimens [1]. Fig. 2 shows the dimensions of the specimens; the total length was 250 mm and the width was 10 mm. Pairs of GFRP tabs were used to reduce the stress when holding each specimen.

The strength of the original CFRP was measured, and used as a reference for the strength of subsequent joints. Five joint types were tested, divided into two groups. One was constructed using dry carbon fabrics and CFRP. In this group, the CFRP half of the joint was manufactured first, and then re-molded again with dry carbon fabric. Fig. 3 shows types 1 and 2 of the first joint group. The left half of both joints was a stepped CFRP portion that had been molded, and the right side represents a dry carbon fabric. We used these to investigate the effects of the number of steps connected to dry carbon fabrics, and therefore the major difference between the two joints is the number of CFRP steps.

The second group was constructed with two dry carbon fiber halves; thus, the whole joint was made in a single step. Fig. 4 shows types 3, 4, and 5 of the second joint group. These joints were named laminated joint-1, laminated joint-2, and multi-overlapped joint, respectively.

Fig. 1. A schematic view of the VARTM process used in this work
increases the contact area, but also increases joint thickness. On the other hand, the remaining two joints were much stronger than the previous four joints. Laminated joint-2 and the multi-overlapped joint had tensile strengths of 26.8 kN (79%) and 28.8 kN (85%), respectively. These two joints performed similarly, with the major difference being the greater thickness of the multi-overlapped joint-2, which could be the reason for the higher observed strength. Löbel et al. [9] constructed CFRP joints based on stainless pins, which resulted in a high joining efficiency of 83%. However, the metal-to-carbon fiber contact caused galvanic corrosion of the carbon fabrics, weakening the structure over time [4].

4. Conclusion
Five adhesive joints were designed using manufacturing process developed from the VARTM process. The tensile test results showed low strength when one half of the joint is CFRP fabrics, which was the case for the first two developed joints. On the other hand, the last two joints, laminated joint-2 and multi-overlapped joint, showed higher tensile strength. However, joining techniques that use dry carbon fibers are still limited for simple shapes, so there are some difficulties for applying these techniques for complex curved shapes like wind blades and lens as well.

References
IMMUNOSUPPRESSION BY COLON CANCER CELLS, MEDIATED BY TUMOR-SECRETED SOLUBLE FACTORS

Moses K. Kamita¹, Arihiro Kano², Shindo Mitsuru²
¹Molecular and Material Science, IGSES, Kyushu University -
²Institute for Material Chemistry and Engineering, Kyushu University

Abstract: In this study, soluble factors secreted by colon cancer cells (CT26) are being investigated. Conditioned medium from cultured CT26 cancer cells was collected and analyzed for the presence of immunosuppressive compound. The presence of the active compound in the samples was constantly monitored by measuring the suppression of IFN-γ expression by ELISA using splenocytes from a normal mouse. Suppressive activity in CT26 conditioned medium was shown to be mediated by a soluble factor(s) that is less than 10kDa. After fractionation with HPLC, suppression of IFN-γ expression was detected in the two different fractions. Further processing of the fractions is needed for the identification of the specific compounds that are responsible for the suppression of tumor immunity.

1. Introduction

The immune system works by distinguishing self from non-self and eliminates the non-self. IFN-γ is a pleiotropic cytokine that is produced primarily by T-cells upon antigen stimulation, and works as an antiviral, as well as an antiparasitic agent in the body. It also inhibits the proliferation of several normal and transformed cells. The production of interferon-gamma (IFN-γ) in splenocyte culture and its suppression by the conditioned medium of tumor cells have previously been reported.

Effective tumor immunotherapy is hindered by a number of obstacles such as the ability of tumor cells to create a tolerant microenvironment, activation of negative regulatory checkpoints in the tumor microenvironment, and secretion of immunosuppressive cytokines and soluble inhibitory factors. Additionally, tumor-associated changes in myelopoiesis that lead to the excessive accumulation of immature myeloid cells in the tumor are thought to play a critical role in tumor-associated immunosuppression. Although this tumor-associated immunosuppression is thought to be driven by soluble factors that are expressed by cancer cells, their identity and mode of action remain largely unknown.

Overexpression of different pro-inflammatory cytokines in tumor conditions have been shown to result in an elevated growth of tumors, as well as other metastatic diseases. In addition, reports have indicated that blocking these cytokines results in significant reduction in the rate of tumor growth. Tumor cells also secrete high amounts of pro-inflammatory cytokines that have the potential to induce a local pro-inflammatory microenvironment. Although these observations are in agreement with the reports that chronic inflammation plays a role in tumor development and progression, there are no much details on the link between these two observations.

CT26 cells are murine colon tumor cells that were developed through exposure of BALB/c mice to N-nitroso-N-methylurethane resulting in a cell line that is easily implanted and readily metastasize. The CT26 model in BALB/c mice has provided a syngeneic test system for developing, as well as testing different immunotherapeutic concepts. Using CT26 cells, this study aimed to identify the soluble factor(s) that suppress the immune response against tumor development. Suppression of IFN-γ production in a splenocyte assay was used as an indicator of the presence of active factors.

2. Material and Methods

Cell Culture. Murine colon tumor CT26 cells were purchased from American Type Culture Collection (ATCC) (Manassas, VA, USA), and maintained with D-MEM (Wako Pure Chemical Industries, Ltd., Osaka, Japan) supplemented with 5% heat-inactivated horse serum in a 5% CO2 atmosphere at 37°C. Balb/c mice were purchased from Kyudo Co. Ltd. (Tosu, Japan) and all animal experiments were carried out according to the guidelines for the proper conduct of animal experiments published by the Science Council of Japan. All experimental protocols were approved by the Ethics Committee and the Animal Care and Use Committee of Kyushu University. Splenocytes were prepared from a spleen of a normal mouse and seeded at one million cells per well in a 96-well culture plate (Thermo Fisher Science Inc., USA), stimulated with lipopolysaccharide and cultured for 24 hours with or without 10% of the test samples.

Conditioned Media Collection and Processing: The tumor cells were cultured to subconfluence, and the medium changed to serum free media. After two days, the medium was recovered and filtered through a 10kDa filter. The filtrate was separated using a C18 Sepak column and the resulting sample fractionated using HPLC. The presence of the active compound in the samples was constantly monitored by measuring the suppression of IFN-γ expression in a splenocyte assay.

Enzyme-linked Immunosorbent Assay (ELISA): Quantification of IFN-γ in conditioned media and fractionated samples was performed by
Various soluble factors have been reported in association with their role in suppressing the immune response against the tumor. These factors include IL-10, TGF-β, galectin-1, gangliosides, PGE₂, G-CSF, and M-CSF among others. Here, the immunosuppressive factor(s) from CT26 cells that is responsible for this activity is a 10kDa molecule. The presence of activity in two separate fractions is an indication that more than one factor is involved in this activity. Although different factors use different mechanisms in different cancer models to suppress the immune system, most of the immunosuppressive factors suppress the immunity through the myeloid-derived suppressor cells (MDSC) by enhancing their proliferation. Small factors such as PGE₂ that can pass through the 10K filter could be involved in the observed activity. However, further analysis is needed to confirm the identity of the compounds.

5. Conclusion

Use of splenocytes isolated from normal mouse facilitated the detection of immunosuppressive factors secreted by tumor cells. Further processing of the fractions is needed for the identification of the specific compounds that are responsible for the suppression of tumor immunity. This identification will pave way for the elucidation of the mechanisms through which tumors evade the immune response. In addition, the information may be help in the development of tumor therapy.

6. References

CATALYTIC PERFORMANCE OF AG-COATED ZEOLITE FOR SOOT OXIDATION

Honcheng Ruan¹, Maiko Nishibori¹

¹Department of Molecular and Material Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuka, Fukuoka 816-8580, Japan; E-Mail : ruanhongcheng@126.com

Abstract: Ag-coated zeolite catalyst (Ag/HSZ890HOA) mixed with candle soot (CS) for 1, 10, 30 and 60 min, exhibited T max (temperature according to highest peak of DTA curves) value of 494, 485, 425 and 376/492 °C for T0-1, T0-10, T0-30, T0-60, respectively. Interestingly, catalyst mixing with CS for 60 min showed two T max peaks on differential thermal analysis (DTA) curves.

1. Introduction

Environmental issues are harmful aspects on human activity on the biophysical environment. Some environmental issues are belong to air pollution, such as Ozone depletion, Global warming, Acid rain, Photocchemical smog and PM 2.5 issue. Diesel particulate matter (PM) consists principally of combustion generated carbonaceous materials (soot) on which some organic compounds have become adsorbed [1]. The research of corresponding catalyst on PM oxidation become more and more important.

2. Experimental

Ag-doped catalysts (4.5%) were prepared by ordinary impregnation of HSZ891HOA, with an aqueous solution of the nitrate salt, AgNO₃. Ag-coated zeolite catalyst (Ag/HSZ890HOA) and candle soot (CS) were mixed by mixing machine instead of mortar for 1, 10, 30 and 60 min, as showed in Fig. 1. The products mixed with CS for 1, 10, 30 and 60 min were denoted as T0-1, T0-10, T0-30, T0-60. Thermogravimetry (TG) and differential thermal analysis (DTA) measurement were carried out for catalytic oxidation of CS. The morphologies of the products were analyzed by scanning electron microscope (SEM).

3. Results and Discussion

Surface morphologies of catalysts mixing with CS for different time (1, 10, 30 and 60 min) were showed in Fig. 2. There just be one exothermic peak corresponding to a weight loss step on TG curves with mix time 1 and 10 min, another one peak appeared with the increasing mix time gradually. Therefore, an obvious double-shoulder peak appeared on catalyst DTA curves after mixing 60 min. Tmax of DTA curves for catalyst Ag/HSZ890HOA are listed in Table 1. SEM images (Fig. 2) showed that the number of broken catalyst particles increased obviously as the increasing mix time from 1 min to 60 min.

Table 1

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<th>Mix time / min</th>
<th>1</th>
<th>10</th>
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<th>60</th>
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<td>T max / °C</td>
<td>494</td>
<td>485</td>
<td>425</td>
<td>376/492</td>
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Fig. 1. TG and DTA curves of candle soot with Ag/HSZ890HOA catalysts in different mix time with mix machine (a-d) 1-60min.
Fig. 2. SEM images of candle soot with Ag/HSZ890HOA catalysts in different mix time with mix machine (a-d) 1-60min.

4. Conclusion

Ag-coated zeolite catalyst (Ag/HSZ890HOA) shows a good catalytic performance. However, a further study about the principle based on two peaks on DTA curves need to be done.

5. References

ATTITUDE AND ALTITUDE STABILIZATION OF OUTDOOR TETHERED QUAD-ROTOR

Tarek N. Dief¹, Shigeo Yoshida²
¹ Department of Earth System Science and Engineering
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Abstract: This paper presents an overview of the most effective ideas for the Quad-rotor project. The concept of modelling using different methods is presented. The modelling part discussed the nonlinear model, and the concept of linearization using small disturbance theory. Parameter identifications part explained the most important parameters that affect the system stability and tried to get suitable solutions for these problems and identify some parameters experimentally. The control part incorporates different classical schemes such as PD and PID controllers to stabilize the Quad-rotor. The difference between the indoor and outdoor controller is presented from the mathematical and the experimental techniques.

1. Introduction
Nowadays, automatic flying of intelligent vehicles moving in space represents a huge field of applications. The rapid development of the microcontroller affects all control’s applications which mean new control theory, new researches, and new challenges. The applications of the hovering aerial vehicles open the door for researchers to present better controllers to achieve more aggressive missions. Nonlinear control theories and applications are the target of the researchers to present or develop more controllers which were very difficult to be implemented using the old microcontrollers. Using the nonlinear model will cancel the assumptions which we make during the control design process; so we will deal directly with the nonlinear model.

A lot of application for the Quad-rotor has been applied especially for the outdoor flights. Civilian application for the UAV includes atmospheric analysis, mapping, maintenance inspection, photography for natural disaster, etc…

2. System Identification and Control Design:

a. System Identification:
In the Quad-rotor model, we were dealing with a fixed model and now we found a problem with the parameters variation, so we need model can make the update of the parameters real time by knowing the history of the plant input also from the system output data.

Placket’s model: This way depends on the least-squares fitting. The concept of this model depends on minimizing the square difference between the predicted output \( Y_m \) from the calculation and between the real data from the sensor data \( Y \) as shown in equation (1):

\[
\text{Mean square error} = \frac{1}{n} \sum_{k=1}^{n} (Y(k) - Y_m(k))^2
\]  (1)

And the following curves show the system open loop transfer function parameters and plotting them online.

Where, the system parameters are shown in equation (2):

\[
\frac{Y(z)}{U(z)} = \frac{b_0 Z^{-1} + b_1 Z^{-2}}{1 + a_1 Z^{-1} + a_2 Z^{-2}}
\]  (2)

Fig.1 system parameter b0 with time

Fig.2 system parameter a1, a2 with time

Also neural network is applied to make the system identification for the system parameters (time series prediction); also this algorithm is better from the Placket’s model. Also the initial values have no effect on the system parameters unlike the Placket’s model.
Also applying the neural network is very important in our application as the outdoor flights will have a high disturbance due to the disturbance flow from different directions. So we can make estimation for the disturbance by modelling the system.

Fig. 3 System response for the actual and estimated data with time

b. Control design:
A PID controller was implemented because its proportional gain aspect decreases the system time to obtain desired state; its integral gain reduces the steady state error, and the derivative gain will increase the stability of the system. For our problem, it becomes a SISO system and we have the controller equation:

\[ G_c = K_p e + K_i \int_0^t e dt + K_d \dot{e} \]  

(3)

After using (SISOTOOL) package in Matlab and choosing the best gains to our system, it can be used in the real model. These gains are for the linear model so it is needed to use these gains with the nonlinear model and compare between the response between the linear and non-linear model and tune it if necessary.

Fig. 4 Block diagram of the Quad-rotor model and controller.

3. Conclusion
This paper presents the control design of outdoor Quad-rotor. This controller is different for the indoor Quad-rotors. The effect of wind and the interaction between the wind and rotor flow generate forces can disturb the system which mean instability. Using different kind of system identifications has advantages and disadvantages, so due to your application and the hardware which you are using will make you chose the suitable algorithm. The classical control is used due to its simplicity in implementation and easier in tuning.

4. References


DIFFERENT NANOSCALE ZERO VALENT IRONS FOR NITRATE-POLLUTED WATER REMEDIATION

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Abstract: In this study, four nanoscale zero valent iron (NZVI) types were characterized and compared for nitrate removal from water. Through batch experiments, it was observed that old-purchased iron (OP-NZVI) had very low nitrate removal efficiency (10%) for more than 8 hours. Treated iron (T-NZVI) removed approximately half of nitrate concentration within 3 hours. Synthesized iron (S-NZVI) successfully reduced the whole amount of nitrate in one hour. Meanwhile, the improved iron (I-NZVI) removed the same amount within 20 minutes, which indicated the highest performance among other NZVIs.

1. Introduction

Nitrate is a well-known hazardous contaminant in groundwater resulting from agricultural runoff, domestic wastewaters, etc. It can be reduced to nitrite causing methemoglobinemia, liver damage, cancer, and so forth [1]. Attributed to high cost effectiveness and reactivity, NZVI had proven its high efficacy and efficiency in nitrate decontamination from wastewater [2, 3]. However, NZVI’s reactivity decreases through aging [4], which requires a certain treatment to decrease the thick passive shell layer of iron (I, II) oxides/hydroxides. This study investigates the effect of optimized treatment process on old-purchased NZVI and compares nitrate removal kinetics between OP-NZVI, T-NZVI, S-NZVI and I-NZVI.

2. Materials and Methods

Ferric chloride, sodium borohydride and ethanol were purchased for NZVI synthesis. Sodium nitrate was used to prepare a reactant stock solution, while pH buffer solution, hydrochloric acid and sodium hydroxide were used for pH adjustment. Nano iron powder was purchased a year ago. Anhydrous copper chloride was used to enhance NZVI.

To produce T-NZVI, the surface of OP-NZVI was washed using 0.1 N HCl solution (10 g iron per 250 mL acidic solution) in 300 mL conical glass flask [5]. The resulting slurry was washed with ethanol then filtered using vacuum filter.

The S-NZVI was prepared according to the following reduction method:

$$4Fe^{2+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^{0} + 3H_2BO_3^- + 12H^+ + 6H_2$$

In this study, the synthesis conditions were optimized based on previous research work [6]. Sodium borohydride (NaBH₄, 98%, 1.1472 M) was introduced into anhydrous ferric chloride (FeCl₃, 0.1434 M) using a roller pump (flow rate 1 L/h) with a volumetric ratio of 1:1 in 500 mL four-neck glass flask. Anoxic condition was kept by continuous flow of nitrogen gas. The reaction mixture was stirred at 250 rpm and maintained at 25 ± 0.5 °C. After reduction, the jet-black iron nanoparticles were vacuum-filtered and washed with deionized (DI) water (>100 ml/g) and anhydrous ethanol three times each. Finally, the slurry was vacuum-filtered and used immediately in batch experiments.

The batch experiments were anaerobically carried out in 500 mL four-neck glass flask using 100 mg/L of nitrate solution and 2 g/L of NZVI as shown in Fig. 1. The resulting mixture was kept at 25 ± 0.5 °C using water bath. At specific given time intervals, 5 mL of solution sample were withdrawn and filtered through a 0.22 μm membrane for analysis of nitrate, nitrite, ammonium, ferrous, total iron and total nitrogen. The off-gas was absorbed by 100 mL acidic solution for analysis of ammonia gas. 50 mg of CuCl₂ was added in one of experiments to enhance nitrate removal (the used iron is denoted as I-NZVI).

Fig. 1. Schematic layout of batch experiment.

Concentrations of nitrogen compounds in solution samples were analysed by UV–vis spectrophotometer. To characterize NZVI, a transmission electron microscopy (TEM), particle size analyser, Brunauer–Emmett–Teller (BET) specific surface area (SSA) analyser. X-ray diffractometer (XRD) were used to determine morphology, particle size, SSA and crystallinity, respectively.

3. Results

<table>
<thead>
<tr>
<th>Property</th>
<th>BET-SSA (m²/g)</th>
<th>Mean aggregate size (nm)</th>
<th>Particle size range (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OP-NZVI</td>
<td>16.3</td>
<td>1388</td>
<td>70-100</td>
</tr>
<tr>
<td>TNZVI</td>
<td>15.2</td>
<td>950</td>
<td>50-70</td>
</tr>
<tr>
<td>SNZVI</td>
<td>61.1</td>
<td>50</td>
<td>20-50</td>
</tr>
</tbody>
</table>

TABLE I CHARACTERIZATION OF NZVIS
Fig. 2. TEM images of (A) OP-NZVI and (B) S-NZVI at resolutions of 100 and 50 nm.

Fig. 3. XRD pattern of (A) OP-NZVI, (B) S-NZVI and (C) spent I-NZVI.

Fig. 4. Nitrate removal kinetics of NZVIs.

Fig. 5. Effect of CuCl$_2$ addition on nitrate removal by NZVI.

4. Illustrations

5. Conclusion
This study distinguished the differences among four types of NZVI, and succeeded to increase nitrate removal efficiency by treatment of OP-NZVI, using freshly-prepared NZVI synthesized under optimized conditions, or enhancing nitrate removal using NZVI with addition of other contaminant via electrocatalytic reactions.

6. References
Abstract: In the present study, we have developed the free surface LBM (FSLBM) algorithm for wave-structure interaction flow problem. Standard Single Relaxation Time (SRT) approximation with the Bhatnagar-Gross-Krook (BGK) collision model were used. In addition, a Smagorinsky Large Eddy Simulation (LES) Model was implemented in order to capture turbulent structure in the flow. From the results, a good agreement was yielded with the published results and it provided a validation benchmark to qualitatively verify the proposed approach.

1. Introduction

The lattice Boltzmann method (LBM) has become an efficient method for modelling and simulating complex fluid flows. Several advantages have shown to be promising with algorithm operations, data locality and computational parallelism [1]. On the other hand, free surface flow problems have been widely used in interdisciplinary research such as in civil engineering and ocean engineering. For instance, in the wave impact on offshore structure, dam breaking, flood waves and others[2]. In this paper, we present the progress of development of interaction water wave by implementing the FSLBM approach.

2. Lattice Boltzmann Method

2.1 LBM Basic

The evolution of the LBM method is described by lattice Boltzmann equation (LBE) with the standard lattice BGK approximation model. This is given by

\[ f_i(x + \mathbf{e}_i, t + \tau_l) - f_i(x, t) = \Omega_i(f(x, t)) \]  

\[ \Omega_i(f(x, t)) = -\omega_l \left[ f_i(x, t) - f_i^{eq}(x, t) \right] + F_i \]  

\[ i \in \{0,1...8\} \] . At each time \( t \), the particle distribution function \( f_i(x, t) \) is located at the lattice node, \( x \) at respective lattice velocity, \( \mathbf{e}_i \), \( \tau_l \): dimensionless relaxation time. Equilibrium particle distribution function, \( f_i^{eq} \) is given by

\[ f_i^{eq}(x, t) = \omega_l \left[ 1 + \frac{\mathbf{e}_i \cdot \mathbf{u}}{c_s^2} + \frac{(\mathbf{e}_i \cdot \mathbf{u})^2}{2c_s^4} - \frac{\mathbf{u}^2}{2c_s^2} \right] \]  

which consider a lattice-dependent constant, \( c_s \)

The macroscopic values for density and velocity of particle distribution function is defined by

\[ \rho(x, t) = \sum f_i \]  

\[ \mathbf{u}(x, t) = \sum \mathbf{e}_i f_i \]  

2.2 LES Smagorinsky Model

Naturally, free surface flows usually occur at very high Reynolds numbers. In the lattice Boltzmann framework, the dimensionless relaxation time is defined by [2]

\[ \tau_{total} = 3 \frac{V^{total}}{c_s^2} + \frac{1}{2} \Delta t = 3 \left( \frac{\tau_g + \tau_l}{c_s^2} \right) + \frac{1}{2} \Delta t \]  

the quadratic equation is obtained as

\[ \tau_l = \frac{1}{2} \left( \sqrt{\frac{2}{\tau_g} + 10 \frac{c_s^2}{\Delta t} \Delta x^2 Q - \tau_g} \right) \]  

Simplification modified relaxation rate, \( \omega_l \) as

\[ \omega_l = \frac{\Delta t}{\tau_{total}} = \frac{\Delta t}{\tau_g + \tau_l} = \frac{2}{\sqrt{\frac{2}{\tau_g} + 10 \frac{c_s^2}{\Delta t} \Delta x^2 Q + \tau_g}} \]  

3. Free surface LBM algorithm

By using FSLBM algorithm proposed by [4], two values will considered to calculate the fluid fraction as given by

\[ \varepsilon = \frac{\mathbf{m}}{\rho} \]  

For an interface cell at \( x \) the mass balance with a neighbor at \( x + \mathbf{e}_i \) is given by [5]

\[ \Delta m_i = \begin{cases} 0 & \text{if } x + \mathbf{e}_i \text{ is gas} \\ 0.5 \cdot [f_i(x + \Delta t \mathbf{e}_i, t) - f_i(x, t)] \cdot [\varepsilon(x + \Delta t \mathbf{e}_i, t) - 1] & \text{if } x + \mathbf{e}_i \text{ is liquid} \\ 0.5 \cdot [f_i(x + \Delta t \mathbf{e}_i, t) - f_i(x, t)] \cdot [\varepsilon(x + \Delta t \mathbf{e}_i, t) - f_i(x, t)] & \text{if } x + \mathbf{e}_i \text{ is interface} \end{cases} \]
the mass for next step can be calculated by adding to the current mass for interface cells from the mass exchange for all directions is defined as
\[ m(x, t + \Delta t) = m(x, t) + \sum_{i=1}^{9} \Delta m_i(x, t + \Delta t) \] (10)
The corresponding free surface boundary conditions will be constructed by [4]
\[ f_{i}^s(x, t + \Delta t) = f_{i}^{(eq)}(\rho_A, \mathbf{u}) + f_{i}^{(eq)}(\rho_A, \mathbf{u}) - f_{i}(x, t) \] (11)

4. Numerical Results
Several numerical simulations were conducted for wave-structure interaction at a high Reynolds number which implemented the D2Q9 LBM model. The present numerical results were compared with an observed experiment and published numerical simulation by [1]. This study used the original configuration of tank size with 45cm x 58cm which was reported by [6]. The computation with domain mesh 464 x 360 was referred to the parameter setting as indicated by [1]. As can be seen from the results, in the early stage, the jet evolved slowly and started to increase gradually to achieve a similar pattern with the previous study in [1]. A limitation to the present study is that it did not consider the gate movement and surface tension effect. Nevertheless, the overall results indicated a qualitatively comparable result with the previous study.

5. Conclusion
In this study, a free surface lattice Boltzmann method (FSLBM) model has been developed to study wave-structure interaction problems. Extension of this work should be considered with Multi-Relaxation Time (MRT) in order to reduce the spurious oscillation. This is a preliminary study using obstacle block. In the future study, we plan to model wave maker algorithm to generate effective water wave.

6. References
STUDY ON DESICCANT AIR-CONDITIONING SYSTEM FOR AGRICULTURAL PRODUCT STORAGE IN PAKISTAN

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Abstract: The present study provides the basic understanding of desiccant air-conditioning (AC) system for storage of agricultural products of Pakistan. In this regard, the study provides the ideal growth zones for various agricultural products. The desiccant air-conditioning applicability has been determined for three different climatic conditions (A, B, C) in order to achieve the sensible and latent load of AC for the studied products. It is determined that desiccant wheel perform higher dehumidification under climatic condition A; because of the maximum ambient air relative humidity. Consequently, higher heat energy is required in climatic condition A to regenerate the desiccant wheel. It has been concluded that the desiccant AC system can be effectively used for agricultural product storage in many regions of Pakistan.

1. Introduction
1.1 Background of products storage
Pakistan is an agriculture based country, blessed with fertile land and four seasons. A huge amount of fruits and/or vegetables in Pakistan is affected due to post-harvest losses, which are about 30-35% and sometimes even more. These losses are mainly due to the mechanical damage, physiological deterioration, and attack of insects and pests

The agricultural products after the harvesting act like living organism and perform respiration, transpiration, ripening processes. Furthermore, these products contain high moisture contents and may spoil within few days after the harvest. Therefore, their shelf or storage life can be increased by retarding the physiological, bio- and chemical changes through control of temperature and relative humidity in the cold storage structure.

1.2 Motivation of the study
The temperature of the cold storage is the most important factor to maintain the quality of the product because the physiological and biological reactions in products which are directly dependant on it. The relative humidity of the storage space is also crucial in controlling the loss of moisture contents from the products and to keep them in good physical and biological appearance [1].

The mechanical refrigeration and/or air-conditioning systems are being used in cold storages for preservation/storage of agricultural products. Besides from other disadvantages of mechanical refrigeration system like environmental degradation, high energy requirements etc., it cannot be used for on farm storage of many tropical fruits and vegetables such as banana, tomatoes, oranges, mangoes, and other leafy vegetables because of chilling injury and discoloration [2]. The standalone evaporative coolers also cannot be used in tropical climatic conditions because of higher relative humidity. On the other hand, the desiccant air conditioning (DAC) system has ability to deal the sensible and latent load of air conditioning distinctly which gives opportunity to use this system for storage of agricultural products efficiently. Therefore, a particular DAC system is proposed in the present study for on-farm pre-cooling or short term storage of tomatoes, sweet-potatoes, watermelon and pears.

2. Ideal storage zone
The tomatoes, sweet-potatoes, watermelon and pears belong to same compatible storage temperature and relative humidity group. The recommended temperature and relative humidity is 18-21°C and 85-90% respectively. The approximate transit and storage life of these products are given in Table I [4]. The ideal storage zone for preservation of tomatoes, sweet-potatoes, watermelons and pears is shown in Fig. 1. The ideal DAC cycle is also drawn on the figure in order to study the system compatibility for the recommended storage conditions.

3. Proposed DAC system
A typical desiccant wheel based DAC system is proposed for the preservation of fruits and vegetables as shown in Fig. 2. Psychrometric model [5] is used to analyse the desiccant wheel performance under three different climatic conditions (A, B, C) of the Pakistan with low regeneration temperature (~40°C). The representative values of temperature and relative humidity of the climatic condition (A, B, C) are given in Table II [4]. The indirect evaporative cooler (IEC) is used to provide the conditioned supply air to the cold storage structure.

<table>
<thead>
<tr>
<th>Table I: Storage life of the studied agricultural products [4].</th>
</tr>
</thead>
<tbody>
<tr>
<td>Products</td>
</tr>
<tr>
<td>Tomatoes</td>
</tr>
<tr>
<td>Sweetpotatoes</td>
</tr>
<tr>
<td>Watermelons</td>
</tr>
<tr>
<td>Pears (ripening)</td>
</tr>
</tbody>
</table>
4. Results and Discussion

The ideal DAC cycle for the climatic condition (A) is drawn on the psychrometric chart as shown in Fig. 1. The inlet air at relative humidity 80% and temperature 24°C passes through the desiccant wheel. The desiccant wheel dehumidifies the air up to 11.96 g/kgDA and increases its temperature as 35.08°C. This air is then entered to the heat exchanger for sensible cooling.

Finally, the air is passed through IEC to supply the sensibly conditioned supply air to the products. The DAC system operates in similar fashion for other climatic conditions (B, C). Therefore DAC cycle for only climatic condition (A) is represented in Fig. 1 to avoid the misunderstanding.

Analysis showed that the desiccant dehumidification capacity increases with increasing regeneration temperature as shown in Fig. 3. Furthermore, desiccant wheel under climatic condition A performs higher dehumidification than other climatic conditions. It is because of higher outdoor air relative humidity. On the other hand, higher heat energy is required to regenerate the desiccant wheel under climatic condition A than the other studied conditions as shown Fig. 4.

5. Conclusion

The DAC system can achieve the thermal conditions required for agricultural products storage in Pakistan at different prevailing climatic conditions. However, its applicability in dry climatic areas is limited.

5. References

THE INVESTIGATION OF THE COLORIMETRY TO MEASURE THE DEPOSITION THICKNESS ON THE PLASMA-FACING WALL IN QUEST


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Abstract: A convenient innovative method named colorimetry is tried to be applied to the Kyushu University Experiment with Steady-state Spherical Tokamak (QUEST) tokamak to measure the film thickness of deposition on the plasma-facing wall. The colorimeter can measure the reflectivity of R-color, G-color and B-color in the same time. The reflectivity is related with the film thickness and complex refractive index of deposition. In this paper, the result of thickness of the deposition measured with colorimeter is compared with that from the reflectivity measured with ellipsometer. They agree quite well with each other. The result shows that it is feasible to apply colorimetry to the measurement of film thickness of deposition. This lays the foundation for the further study of application of colorimetry to the QUEST tokamak.

1. Introduction
For a future nuclear fusion reactor, the characteristics of the plasma-facing wall including the information of the deposition are studied for understanding those such as tritium storage or the hydrogen recycling [1]. The deposition thickness is usually measured with TEM and ellipsometer. But these two heavy devices are very difficult to be applied to the actual plasma-facing wall directly. Because of the convenience, the colorimeter can measure the deposition thickness on the actual plasma-facing wall easily.

About the measurement of deposition thickness the colorimetry is in good agreement with the ellipsometry for a-C:H (amorphous hydrogenated carbon) dominant deposition in TEXTOR [2]. But for the metal first wall and divertor in ITER, the deposition will contain metals and will not a-C:H dominant any more. And for QUEST the first wall is stainless steel and the divertor and limiter are tungsten. After several campaigns the deposition has been formed on the plasma-facing wall. The main ingredient is the mixture of carbon and metal. It is necessary to study the feasibility of the colorimetry on measuring the metal-containing deposition thickness.

2. The colorimeter
1. Measuring data RGB (Red, Green, Blue) reflectivity.
2. Response range: R (590–720 nm), G (480–600 nm), B (400–540nm).
3. Sensor diameter: 8.1 mm.
4. Diameter of the integrating sphere: 47 mm.
5. Light source: white LED.
6. The reflectivity of light is output as RGB values (0–1023).

\[
\begin{align*}
I_R &= I_{R0} \times e^{-\frac{\pi}{\lambda_0} n R^2} \\
I_G &= I_{G0} \times e^{-\frac{\pi}{\lambda_0} n G^2} \\
I_B &= I_{B0} \times e^{-\frac{\pi}{\lambda_0} n B^2}
\end{align*}
\]

(1)

(2)

(3)

3. The principle of measurement with the colorimeter

Fig. 1. The principle of measurement of deposition thickness with colorimeter

\[
\begin{align*}
\Delta \lambda &= \frac{2\pi}{\lambda_0} n_i \cos \lambda i \\
n_i &= \frac{n_i \cos i o - n_i \cos i l}{n_i \cos i o + n_i \cos i l} \\
\Delta \lambda &= \frac{n_i \cos i o - n_i \cos i l}{n_i \cos i o + n_i \cos i l} \\
\Delta \lambda &= \frac{n_i \cos i o - n_i \cos i l}{n_i \cos i o + n_i \cos i l} \\
\Delta \lambda &= \frac{n_i \cos i o - n_i \cos i l}{n_i \cos i o + n_i \cos i l} \\
\Delta \lambda &= \frac{n_i \cos i o - n_i \cos i l}{n_i \cos i o + n_i \cos i l}
\end{align*}
\]

(4)

(5)

(6)

(7)

(8)
According to the equations from (4) to (9), if the incident angle $i_0$ and the complex refractive index of support $n_2$ have been known (For QUEST, the support is stainless steel) and it is in the air, so there is

$$R = f(n_1, d_1)$$

(11)

The colorimeter can measure the reflectivity $R$. If the complex refractive index of deposition $n_1$ has been known, then the deposition thickness $d_1$ could be derived.

4. The measurement of complex refractive index of deposition on the QUEST wall with samples

![Image](Fig. 2. The samples on the first wall of QUEST)

Fig. 2. The samples on the first wall of QUEST

![Image](Fig. 3. The T1, T2, T3, T4 and B15 measured with TEM)

Fig. 3. The T1, T2, T3, T4 and B15 measured with TEM.

These samples could be measured with ellipsometer and TEM so that the complex refractive index of deposition could be studied.

![Image](Fig. 4. The measurement principle of the complex refractive index of deposition with ellipsometry)

Fig. 4. The measurement principle of the complex refractive index of deposition with ellipsometry.

According to the equations from (4) to (9), and then there is

$$\tan \Psi e^{-ikd} = f(n_1) = f(n_1, d_1)$$

(15)

The $\Psi$ and $\Delta$ could be measured with ellipsometer directly. The $n_1$ is the deposition’s complex refractive index which contains two parameters, refractive $n_1$ and extinction coefficient $k_1$. The $n_e$ is the sample’s complex refractive index. If the $d_1$ has been measured with TEM, then the $n_1$ could be derived.

5. The complex refractive index of the samples and the deposition of T1, T2, T3, T4 and B15

The three maximum sensitive wavelengths of RGB colorimeter have been chosen to calculate the complex refractive index of deposition.

![Image](Fig. 5. The complex refractive index of the 21 samples and the deposition of T1, T2, T3, T4 and B15)

Fig. 5. The complex refractive index of the 21 samples and the deposition of T1, T2, T3, T4 and B15

6. Conclusion

From the distribution of complex refractive index of 21 samples, it is presented that on the plasma-facing wall of QUEST there are three regions in which the optical characteristic of deposition is different. In the upper side and lower side, we need do more experiment of TEM to get more complex refractive index of deposition, so that we can get right complex refractive index which could be applied to the colorimetry.

7. References


NUMERICAL STUDIES OF NATURAL VENTILATION OF BUILDING WITH LEEWARD OPENINGS

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Abstract: Ventilation is a process of changing air in an enclosed space. Air should continuously be withdrawn and replaced by fresh air from a clean external source to maintain internal good air quality, which may referred to air quality within and around the building structures. In this work, computational simulation is performed on a real-sized box-room with dimensions 5 m x 5 m x 5 m. Two opening of the total area 4 m² are differently arranged, resulting in 4 configurations to be investigated. A logarithmic wind profile upwind of the building is employed. A commercial Computational Fluid Dynamics (CFD) software package CFD-ACE of ESI group is used. A Reynolds Average Navier Stokes (RANS) turbulence model & LES turbulence model are used to predict the air’s flow rate and air flow pattern. The governing equations for large eddy motion were obtained by filtering the Navier-Stokes and continuity equations.

1. Introduction

Natural ventilation is the process of supplying and removing air through an indoor space without using mechanical systems. In developed countries, most of the buildings are responsible for 1/3 of all energy consumption e.g. in US, about 30% of total energy consumption is used in non-domestic buildings, and of that fraction about 30% is used in heating and cooling [1], [2], [3].

Single-sided ventilation has fewer adaptive comfort hours than two-sided ventilation and produces much less ventilation volume [4] is used when there is non-availability of other choice.

The reliable methods of getting information about the air flow and pressure distribution around and inside the building are through full scale measurements [5], scale model testing using wind tunnel [6] and computational fluid dynamics (CFD) [7, 8].

The common CFD techniques are direct numerical simulation (DNS), large-eddy simulation (LES) and Reynolds averaged Navier-Stokes (RANS) equation with turbulence models. Each technique handles turbulence in different ways [9, 10]. Among those techniques, RANS is widely used by most CFD software [11], however, LES should be more suitable than the RANS approach to study highly three-dimensional or separated flows, especially those in which the gradient transport hypothesis, and consequently one and two-equation models of turbulence, fails [12]. It was introduced by Dearsdoff in the early 1970s [13] for meteorological applications.

The present investigation is focused on the application of three dimensional RANS and LES modeling on wind driven natural ventilation of double openings at single-sided buildings.

2. Methodology

This study involves 4 configurations models of leeward double opening (Figure 1). The dimensions of the building-like models are 5 m x 5 m x 5 m. The computational domain constructed had a height of 4H, width of 9H and length of 13H (H=5m), sufficiently large to avoid disturbance of air flow around the building [14]. A logarithmic wind profile upwind of the building is employed.

The commercial software package CFD-ACE from the ESI group is used for the computation.

2. Result & Discussion

The present results is about the study of the flow patterns and air flow rate using RANS and LES scheme when modelling wind driven natural ventilation in buildings. The velocity components have been determined, along streamwise and vertical direction, respectively. LES is used to compare with RANS as LES is produced more precise results but more time-consuming method [15].

Figure 1 shows the air flow pattern inside the building. The opening is marked as A and B, where the air enters the building through the lower opening A and comes out through the upper opening B. If the level of the opening is at the same height, the air will enter through the lower area and come out through the upper area of both openings.

Table 1 shows numerical values of air flow rate of simulation that being performed at University of Technology, Sydney. Each configuration gives different flow rate and it is found that the highest flow rate occurs at configuration a(iv) for RANS and a(ii) for LES, whereas the lowest flow rate occurred at configuration a(i) for both RANS and LES.

4. Conclusion

In this recent study, RANS and LES approaches have been applied to wind driven natural ventilation in a cubic building. Both RANS & LES scheme give almost the same air flow rate with the difference between 4-8%. The location & arrangement of opening influences the air flow rate and air flow pattern.
Table 1. Numerical values of airflow rate

<table>
<thead>
<tr>
<th>Opening Configuration</th>
<th>Airflow rate (m³/s)</th>
<th>RANS</th>
<th>LES</th>
</tr>
</thead>
<tbody>
<tr>
<td>a(i)</td>
<td>6.63 x 10⁻¹</td>
<td>6.09 x 10⁻¹</td>
<td></td>
</tr>
<tr>
<td>a(ii)</td>
<td>6.91 x 10⁻³</td>
<td>7.46 x 10⁻³</td>
<td></td>
</tr>
<tr>
<td>a(iii)</td>
<td>6.52 x 10⁻³</td>
<td>7.10 x 10⁻³</td>
<td></td>
</tr>
<tr>
<td>a(iv)</td>
<td>7.45 x 10⁻³</td>
<td>7.15 x 10⁻³</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1 Double Opening on Leeward Wall

5. References
STATISTICAL EVALUATION OF COMPRESSION INDEX CORRELATIONS

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Abstract: Primary consolidation of cohesive soil can significantly affect the serviceability of overlying structures and its amount is calculated using the compression index (Cc). Determination of Cc is complex and time consuming that raised the need for using empirical correlations with simpler tests. Development of these correlations started as early as the 1940s and new correlations still being developed. Most of these correlations were derived using data fitting with site-specific measured values and was evaluated using simple statistics. Better statistical evaluation may reduce the correlation deviation. ATIC method in-line with other evaluation measures was used to evaluate 92 compression index correlations using measured data from Egypt, UAE, Iraq, and Indonesia. For the studied data, each statistical measure ranks the correlations differently, especially for the best correlation. The advantages and shortcomings of each statistical measure were briefly introduced.

1. Introduction

Soil compressibility can significantly affect the serviceability of the overlying structures [1]. For cohesive soil; primary consolidation has the most significant effect that is estimated using compression index (Cc). Determination of Cc is complex and time consuming that made empirical correlations more important. Many correlations were developed to estimate Cc for different soil conditions as early as the 1940s and new correlations still being developed [2].

Most of these correlations were derived from data fitting of measurements at specific site conditions that may cause large deviation if used for other sites [3]. Better statistical evaluation may reduce the overall deviation of the geotechnical parameter and enhance the overall assessment.


Most of the commonly used statistical evaluation measures had shortcomings that it considers position conformity or trend conformity separately. This shortcoming may cause misjudgement of the correlation. This paper evaluates 92 Cc correlations using commonly used statistical measures and Amended Theil Inequality Coefficient (ATIC) method as presented by Song et al. [8]. ATIC method has the advantage that it takes into account both position and trend conformities in the overall evaluation process.

2. Used Data

Subsurface investigation reports were collected from Egypt, UAE, Iraq, and Indonesia and entered into customized geotechnical database. Data for this study was collected with the condition that the sample has all needed parameters to insure consistency and accuracy of the evaluation process. Table 1 shows descriptive statistical measures for the used soil properties.

3. Used Correlations

Several correlations were developed to correlate the Cc with field state and intrinsic properties as in Table II. Total of 92 correlations were considered in this study.

<table>
<thead>
<tr>
<th>Property</th>
<th>Range</th>
<th>Mean</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Voids Ratio</td>
<td>0.32 - 4.35</td>
<td>1.58</td>
<td>0.84</td>
</tr>
<tr>
<td>Bulk Density t/m³</td>
<td>1.04 - 2.29</td>
<td>1.61</td>
<td>0.31</td>
</tr>
<tr>
<td>Water Content (%)</td>
<td>11.9 - 168.12</td>
<td>57.15</td>
<td>31.09</td>
</tr>
<tr>
<td>Liquid Limit (%)</td>
<td>17.1 - 166.2</td>
<td>62.68</td>
<td>25.22</td>
</tr>
<tr>
<td>Plasticity Index (%)</td>
<td>2.48 - 113.9</td>
<td>30.71</td>
<td>17.84</td>
</tr>
<tr>
<td>Compression Index</td>
<td>0.07 - 1.66</td>
<td>0.57</td>
<td>0.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TABLE II</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Correlation with single soil property</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor.ID</td>
<td>Formula</td>
<td>Cor.ID</td>
<td>Formula</td>
</tr>
<tr>
<td>C01</td>
<td>Cc = 0.158 - 0.27</td>
<td>C27</td>
<td>Cc = 0.0714 - 0.12</td>
</tr>
<tr>
<td>C02</td>
<td>Cc = 0.166 + 0.0107</td>
<td>C28</td>
<td>Cc = 0.0035 - 0.25</td>
</tr>
<tr>
<td>C03</td>
<td>Cc = 0.11 + 0.5 - 1.87</td>
<td>C29</td>
<td>Cc = 0.0635 - 0.10</td>
</tr>
<tr>
<td>C04</td>
<td>Cc = 0.35 - 0.5</td>
<td>C30</td>
<td>Cc = 0.00714</td>
</tr>
<tr>
<td>C05</td>
<td>Cc = 0.15 + 0.25</td>
<td>C31</td>
<td>Cc = 0.0216</td>
</tr>
<tr>
<td>C06</td>
<td>Cc = 0.14 + 0.23</td>
<td>C32</td>
<td>Cc = 0.0158 - 0.20</td>
</tr>
<tr>
<td>C07</td>
<td>Cc = 0.41 + 0.25</td>
<td>C33</td>
<td>Cc = 0.0141 + 0.02</td>
</tr>
<tr>
<td>C08</td>
<td>Cc = 0.156 + 0.425 - 0.94</td>
<td>C34</td>
<td>Cc = 0.0125 + 0.044</td>
</tr>
<tr>
<td>C09</td>
<td>Cc = 0.153 - 0.138</td>
<td>C35</td>
<td>Cc = 0.0141 - 0.165</td>
</tr>
<tr>
<td>C10</td>
<td>Cc = 0.0286 + 0.0083</td>
<td>C36</td>
<td>Cc = 0.0047 + 0.165</td>
</tr>
<tr>
<td>C11</td>
<td>Cc = 0.75 + 0.5</td>
<td>C37</td>
<td>Cc = 0.0153</td>
</tr>
<tr>
<td>C12</td>
<td>Cc = 0.215 + 0.125</td>
<td>C38</td>
<td>Cc = 0.0151</td>
</tr>
<tr>
<td>C13</td>
<td>Cc = 0.15 + 0.35</td>
<td>C39</td>
<td>Cc = 0.0151 - 0.794</td>
</tr>
<tr>
<td>C14</td>
<td>Cc = 0.15 + 0.91</td>
<td>C40</td>
<td>Cc = 0.0151</td>
</tr>
<tr>
<td>C15</td>
<td>Cc = 1.154</td>
<td>C41</td>
<td>Cc = 0.0151</td>
</tr>
<tr>
<td>C16</td>
<td>Cc = 0.14 + 0.37</td>
<td>C42</td>
<td>Cc = 0.0001266 + 0.0000933 - 0.0135</td>
</tr>
</tbody>
</table>

Table II: Total of 92 correlations were considered in this study.
4. Correlations Evaluation

Current correlation evaluation measures consider position and trend conformities separately that may lead to misjudgment and wrong selection. The ATIC method as proposed by Song et al. [8] has the advantage that it considers both position and trend conformities.

Table IV shows the 5 top-most and bottom-most ranked correlations based on ATIC method using the procedure given in [8]; $R^2$ and MAD values based on the equations given in [2]; RMSE value based on the equation given in [7]; and RI and RD values based on the procedures given in [4].

### Table V

<table>
<thead>
<tr>
<th>Rank</th>
<th>ATIC</th>
<th>$R^2$</th>
<th>MAD</th>
<th>RMSE</th>
<th>RI</th>
<th>RD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C22</td>
<td>0.39e</td>
<td>0.013</td>
<td>0.011</td>
<td>0.85</td>
<td>0.12</td>
</tr>
<tr>
<td>2</td>
<td>C80</td>
<td>0.37e</td>
<td>0.013</td>
<td>0.011</td>
<td>0.85</td>
<td>0.12</td>
</tr>
<tr>
<td>3</td>
<td>C43</td>
<td>0.46e</td>
<td>0.013</td>
<td>0.011</td>
<td>0.85</td>
<td>0.12</td>
</tr>
<tr>
<td>4</td>
<td>C30</td>
<td>0.39e</td>
<td>0.013</td>
<td>0.011</td>
<td>0.85</td>
<td>0.12</td>
</tr>
<tr>
<td>5</td>
<td>C50</td>
<td>0.50e</td>
<td>0.013</td>
<td>0.011</td>
<td>0.85</td>
<td>0.12</td>
</tr>
<tr>
<td>91</td>
<td>C62</td>
<td>0.21e</td>
<td>0.013</td>
<td>0.011</td>
<td>0.85</td>
<td>0.12</td>
</tr>
<tr>
<td>92</td>
<td>C15</td>
<td>0.13e</td>
<td>0.013</td>
<td>0.011</td>
<td>0.85</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Where: $e$: voids ratio, $n$: porosity; $\gamma_d$: dry density (g/cm$^3$); $I_r$: liquid limit; $W_c$: natural water content; $G_s$: specific gravity

5. Conclusion

Total of 92 compression index correlations were evaluated using commonly used statistical measures in-line with ATIC method. The results show that each statistical measure gave different ranking for the correlations. ATIC method has the advantage that it considers both position and trend conformity in the evaluation process. $R^2$ has the shortcoming that it considers only the trend of the values without considering their relative position. MAD and RMSE values have the shortcoming that they evaluate only the values’ position around the average. The RI considers only the position of the data. The RD is biased for the odd ratios between the correlated and observed values.

Acknowledgments

Waled A. Daoud would be thankful to the Egyptian Ministry of Higher Education (MoHE) and EJUST for funding his PhD studies and special thanks to Kyushu University for offering the tools and equipment needed for the research.

References

HETEROJUNCTION DIODE OF NITROGEN-DOPED ULTRANANOCRYSTALLINE DIAMOND FILMS PREPARED BY COAXIAL ARC PLASMA DEPOSITION

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Abstract: Nitrogenated ultrananocrystalline diamond/hydrogenated amorphous carbon composite films were prepared in atmospheres of nitrogen and hydrogen mixed gases, by coaxial arc plasma deposition method. Effect of nitrogen incorporated to the films was electrically investigated. The nitrogen-doped films possesses n-type semiconductor, it was confirmed by studying the heterojunction of the film with p-Si. I-V curve of the junction exhibited a high rectifying action in room temperature. The obtained results confirm that the Nitrogen-doped ultrananocrystalline diamond/hydrogenated amorphous carbon composite film is a good candidate material for the electronic device applications.

1. Introduction

Diamond like carbon (DLC) materials have been of considerable interest to many researchers in recent years, mainly due to their amorphous nature which opens up a possibility of incorporating of other elements such Si, F, P, Ag and N\textsuperscript{1,2} which upgrades its application in the field of semiconductor technology. However, the high-density defects and complex structure negatively effect on the doping process; accordingly limit their applications on the electronic devices.

On the other hand, semiconducting ultrananocrystalline diamond/hydrogenated amorphous carbon composite (UNCD/a-C:H) films have a specific structure, wherein a large number of diamond crystallites of less than 10 nm diameter are embedded into an a-C:H matrix. These films are applicable to biomedical, mechanical and electronics applications\textsuperscript{3,4} because of their advantageous features including their unique optical and electrical properties. It has been experimentally proved that the UNCD/a-C:H films, prepared by pulsed laser deposition (PLD)\textsuperscript{5} and coaxial arc plasma deposition\textsuperscript{6} possess large optical absorption coefficients. This property mainly attributed to the UNCD grain boundaries\textsuperscript{7}.

UNCD/a-C:H films attract many researchers due to the possibility of realizing n-type and p-type conduction by Nitrogen and Boron doping, respectively\textsuperscript{8,9}. Concerning nitrogen-incorporated UNCD, Bhattacharyya \textit{etaal}\textsuperscript{10} have reported that UNCD films can be doped with nitrogen to achieve a conductivity of 143 S/cm by chemical vapor deposition (CVD) method. In our group, we succeed to grow nitrogen-doped UNCD by PLD method\textsuperscript{11}, and it is experimentally proved that the electrical conductivity of the film is enhanced with increasing nitrogen contents, the enhancement of conductivity with nitrogen doping was attributed to the change of structure properties of films for both, CVD\textsuperscript{12}, and PLD\textsuperscript{8,11} methods.

In this letter, we report heterojunction diodes comprising nitrogen-doped UNCD/a-C:H and p-type Si and fabricated by coaxial arc plasma deposition method. The heterojunction performance was evaluated based on current–voltage (I–V) measured in dark at room temperature.

2. Experimental details

UNCD/a-C:H films were deposited on p-type Si (100) substrates at a substrate temperature of 550 °C in a nitrogen and hydrogen mixed gas atmosphere of 53.3 Pa by coaxial arc plasma deposition (CAPD) with a coaxial arc plasma gun equipped with a graphite target\textsuperscript{6}. The CAPD apparatus was evacuated down to a base pressure of less than 10Pa using a turbo molecular pump, and then hydrogen and nitrogen gas was fed into the apparatus at a total inflow rate of 10 sccm. Heterojunction was formed by depositing nitrogen doped UNCD and p-type Si by radio frequency (RF) sputtering. Pd electrode was deposited on both sides for ohmic contact.

3. Results and Discussion

Formation of diamond grains by CAPD compared with that by CVD has the following major differences: (i) lower substrate temperatures, (ii) much higher deposition rates, and (iii) no requirement of substrate pretreatment using diamond powder.

![Fig. 1. Schematic of coaxial arc plasma deposition (CAPD) system.](image-url)
From these differences, the formation mechanism by CAPD should be greatly different from that by CVD. Schematic of coaxial arc plasma deposition (CAPD) system is shown in Fig.1. UNCD/a-C:H films have electrically insulating properties. In contrast, 3 at. % nitrogen content UNCD/a-C:H films deposited of hydrogen and nitrogen gases are electrically conductive.

In order to illustrate the conduction type of nitrogen-doped UNCD/a-C:H films, heterojunction diodes have been manufactured by depositing films on p-type Si substrates, as shown in Fig. 2. To provide better understanding of these heterojunction properties, dark I–V curves of the diodes measured in dark at room temperature, as shown in Fig.3. I–V curve exhibited a rectifying action similar to that of conventional p-n heterojunctions with a rectification ratio of more than $10^4$ for bias voltage of ±1 V. The obtained results suggest n-UNCD/a-C:H as a promising candidate to be applied in electronic and optoelectronic devices.

**Fig. 3. Current-Voltage characteristics of the heterojunction diode. Inset is linear scale.**

4. **Conclusion**

3 at. % nitrogen-doped UNCD/a-C:H film deposited by CAPD method possessed n-type conduction and easily forms junction with p-type semiconductor.

5. **References**

ULTRANANOCRYSTALLINE DIAMOND/AMORPHOUS CARBON COMPOSITE FILMS SYNTHESIS ON CEMENTED CARBIDE SUBSTRATE BY COAXIAL ARC PLASMA DEPOSITION

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2 Department of Applied Science for Electronics and Materials, Kyushu University, Japan, 3 OSG Corp., Japan

Abstract: Ultrananocrystalline diamond/amorphous carbon composite films, wherein a larger number of diamond grains with diameters of less than 10 nm are embedded in an amorphous carbon matrix, were deposited on cemented carbide (WC-6wt.% Co) substrates by using coaxial arc plasma deposition at different repetition rates and deposition temperatures. The hardness and Young’s modulus were measured by nanoindentation. The film deposited at a repetition rate of 1 Hz and room temperature exhibited the maximum hardness of 51 GPa and modulus of 520 GPa. This implies that catalytic effects of Co in the WC-Co substrates, which induce the graphitization of the films, can be suppressed by the low deposition temperature, since the catalytic effects are enhanced with increasing temperature.

Key words: Nanodiamond, Hard coating, Coaxial arc plasma deposition, CAPD, Nanoindentation, Cutting tools

1. Introduction
Hard coating can give functions such as enhanced hardness, chemically stable surface, and thermal protection to mechanical tools, particularly lengthen the lifetime of the tools. Cathodic arc discharge has ever been employed for the deposition of sp2-rich amorphous carbon film coatings [1], since this method can provide highly energetic carbon ions, which is indispensable for the formation of sp3 bonds, onto substrates [2-4].

In addition to the merits of cathodic arc discharge, coaxial arc plasma deposition (CAPD) has the following distinctive feature: a coaxial arc plasma gun is equipped with an anodic cylinder that can bunch ions ejected from a cathodic graphite rod located inside the cylinder. Owing to this structure, a supersaturated condition with highly energetic ions can be realized, which is desired for the growth of ultrananocrystalline diamond (UNCD) crystallites [5]. CAPD can form ultrananocrystalline diamond/amorphous carbon composite (UNCD/a-C) films without the pre-treatment of substrates with diamond powder [6]. A high hardness of UNCD/a-C films are attributed to the coexistence UNCD grains and sp3-rich a-C [7].

Cemented carbide (WC-6wt.% Co), which is a typical cutting tool substance, contains Co that induce graphitization of diamond. Since the substrate temperature is increased, the catalytic effects of Co is enhanced [8-10], polycrystalline diamond coating by chemical vapour deposition is made after the preferential etching of the Co. CAPD make possible the deposition of UNCD/a-C:H films at low temperature without the pre-treatment of substrates. The process and condition of deposition are completely different between CAPD and CVD.

In this study, the validity of employing CAPD for UNCD/a-C coating is investigated, and the influences of cemented carbide substrates on the film growth and mechanical properties were mainly discussed.

2. Experimental procedures
UNCD/a-C films with thicknesses of 2-3 μm were deposited on cemented carbide plate substrates with dimensions of 10 mm diameter and 4 mm thickness by CAPD with a graphite target. As shown in Fig. 1, the film was not peeled off. The main conditions of samples are summarized in Table 1. The films surfaces were observed by scanning electron microscopy. The hardness and Young’s modulus of the films were measured by nanoindentation.

![Fig.1. Optical images of (a) uncoated and (b) UNCD/a-C-coated cemented carbide plate substrates.](image)

<table>
<thead>
<tr>
<th>TABLE I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical preparation conditions.</td>
</tr>
<tr>
<td>Substrate Temp. [°C]</td>
</tr>
<tr>
<td>Repetition Rate [Hz]</td>
</tr>
</tbody>
</table>

3. Results and discussion
Fig.2 shows the X-ray diffraction pattern of the films. Diffraction rings due to diamond-111 and 220 are observed, which evidently indicates the formation of UNCD grains in the films.

Whereas the film (sample 1) deposited at 550 °C and 5 Hz exhibited 17.3 GPa hardness, films deposited on Si substrates at the same conditions exhibited approximately 30 GPa. This reduction in hardness should be attributed to the catalytic effects of Co containing in the cemented carbide [8-10].
The film deposited at room temperature and 5 Hz (sample 2) exhibited 31.8 GPa hardness and 294 GPa Young’s modulus. At the low substrate temperature, as shown in Fig. 3, the hardness and Young’s modulus are obviously enhanced, which implies that graphitization due to the Co catalytic effects are suppressed at the low substrate temperature.

Figure 4 shows typical SEM images of the film surfaces. The films deposited at 550 °C (sample 1) obviously comprises large grains as compared with those of sample 2, which might come from the graphitization.

The film deposited at room temperature and 1 Hz (sample 3) exhibits 51.3 GPa hardness and 520 GPa Young’s modulus. Both hardness and modules are evidently enhanced with decreasing repetition rate of discharge from 5 to 1 Hz. The long interval time 1 s at 1 Hz is advantageous from the viewpoints of cooling. In other words, an increase in the effective substrate temperature might be suppressed at 1 Hz owing to the long interval time, since highly energetic species are arrived at the substrate and the effective temperature on the substrate surface should temporally be increased.

4. Conclusion
UNCd/a-C films were deposited on cemented carbide substrates containing Co by CAPD. It was found that the low temperature growth is effective for suppressing the graphitization due to the Co catalytic effects and CAPD, that makes the low temperature growth possible, is a promising method for the hard coating applications of UNCD/a-C on cemented carbide.

Acknowledgments
This work was partially supported by Osawa Scientific Studies and Grants Foundation.

References
ORTHOGONAL FLUXGATE GRADIOMETER SENSOR AND ITS APPLICATION IN PARTICLE DETECTION

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Abstract: A novel method for constructing an integrated gradiometer and magnetometer is proposed based on Fundamental Mode Orthogonal Fluxgate (FM-OFG) operation. In the integrated sensor construction, the summation of both sensor head outputs is used for the magnetometer operation and the subtraction of them is used for the gradiometer operation. The baseline separation distance between the sensor heads is adjustable. The sensor heads pair can be configured either axially or in parallel. Experiments were conducted with axial configuration of 5 cm baseline to show the selective detection capability to gradient and homogeneous magnetic field. The sensing system presented can be used to measure the average and the gradient of input magnetic field and its interesting applications are the gradiometric sensing of magnetic field distribution anomalies in relatively large homogenous magnetic field interference.

1. Introduction
The gradiometer is a sensor to detect the gradient of the magnetic field. There are two methods to make the gradiometer. One method is electronic; where two identical magnetometers are used and the gradient is obtained by subtracting one magnetometer’s output from the other’s. However, an obvious drawback with the electronic gradiometer is that two complete magnetometers are needed and that a wide dynamic range with a good linearity is needed for the high resolution measurement. The other method uses a single sensor head and is able to obtain the difference of magnetic fields at two specific points. A common structure of this type of gradiometer heads uses two pickup coils wound on a single core [1]. The system becomes compact and can be built with a single driving and detection electronic set, however the base line is fixed and making a good balance between two pickup coils to suppress uniform magnetic field is not easy.

So in order to build a gradiometer having positive aspects of both methods, we propose a new method for building a gradiometer based on the fundamental mode orthogonal fluxgate (FM-OFG) mechanism as shown in Fig. 1 [2]. The proposed FM-OFG gradiometer is composed of two identical sensor heads having hairpin-shaped amorphous wire core with a pickup coil wound around it. The pickup coils of the two heads are connected in counter series; thus allowing the differentiation of the signal on the sensor head level. The proposed configuration allows the gradiometer to have the advantage of a flexible baseline while minimizing the used electronics set and also allowing more amplification of the measured signal. The developed gradiometer heads show high suppression ratio of uniform magnetic field noise and has high sensitivity to magnetic field gradients; which demonstrates the sensor capability of being implemented in various applications for measurement of small magnetic field gradients.

One of the applications for the FM-OFG gradiometer is the detection of magnetic particles in unshielded environment [3]. The developed prototype particle detection system offers size, cost and weight reduction as compared to existing particle detection systems. The system has been investigated numerically to optimize various design parameters of the system. Experimental setup has been developed to evaluate some of the numerically predicted results. Steel balls were successfully detected down to the diameter of 50 µm.

2. Experimental Setup
An illustration of the sensor construction is shown in Fig. 1. The gradiometer head is composed of two FM-OFG heads of length 30 mm. Each sensor head has amorphous wire core of 120 µm diameter. A pick up coil wound on each core, where the pickup coils of both heads are connected in counter series. The excitation current is applied to the amorphous wire core of both heads in series. Figure 2 shows the fabricated gradiometer head. The excitation current has 40 mA dc bias current and 100 kHz ac current of 12 mA root-mean-square, which establishes the fundamental mode operation.

Fig. 1. Schematic sensor circuit

Fig. 2. FM-OFG gradiometer with plastic protection cover
The experimental setup of the magnetic particle detection system is realized based on the considerations taken from the results of the system numerical analysis. The two heads of the gradiometer are fixated in parallel configuration with an 8 mm separation baseline, which is the minimum baseline considering that each sensor head is placed inside a plastic casing of radius 4 mm for protection of the pickup coil and the amorphous wire core. The plastic casing of the sensor head also limits the minimum lift-off to 5 mm with a 1 mm clearance between the moving particle and the sensor case. Magnetic particle samples are prepared using steel balls of diameters 160 μm, 120 μm, 70 μm and 50 μm in order to evaluate the detection system performance. The particles are pre-magnetized using a neodymium magnet and then placed on the rotating table for the gradiometer to measure the remnant magnetization. For a particle to be detectable, the magnitude of the output signal should be higher the sensor noise level taken to be 0.5 nT/m at 1 Hz from Fig. 3. To maximize the amplitude of the measured flux gradient, the particles are placed on the rotating table such that they pass at 2.5 mm to the inner side from the tip of each sensor head. The output signal of the sensor electronic circuit is amplified 400 times and passed on low pass filter of 20 Hz cutoff frequency and High pass filter of 2 Hz cutoff frequency.

3. Results and Discussion
The application of magnetic particle detection using FM-OFG gradiometer is affected by various design parameters. Hence, numerical analysis of the system using finite element method (FEM) has been conducted to determine the optimized values to be used in the construction of the experimental setup. In Fig. 3, the picked up magnetic field gradient by the gradiometer is shown for the variation of the particle position for x, y, and z dipole moment directions. For the x direction dipole moment, the maximum amplitude of the measured signal is around a quarter of that of the y and z direction dipole moments. Hence, to improve detection capability of the sensor, it will be more convenient to pre-magnetize the sample particles in y or z directions. At midway of particle movement, i.e. the particle is situated at midpoint of the baseline separation distance; the y direction dipole achieves the maximum signal amplitude, while the z dipole induces equal axial flux in the same direction to both heads; which leads to omission of the axial flux density gradient.

Experimental results from the detection system prototype are shown in Fig. 4. The 160 μm and 120 μm particles show the y direction magnetization dipole waveform pattern, while the 70 μm and 50 μm particles are showing the z direction one. At the specified lift-off distance, i.e. 5 mm, the 50 μm particle was detectable at a peak output value of 4 nT/m and a signal to noise ratio of 5, which is comparable to recently reported results for a superconducting quantum interference device (SQUID) detection system with magnetic shielding, where a 50 μm particle was detected with signal to noise ratio of 10 at 3 mm lift-off distance.

Fig. 4. Gradiometer output [T/m] for steel balls of diameters 160 μm, 120 μm, 70 μm and 50 μm

4. Conclusions
New magnetic particle detection system in unshielded environment was proposed using FM-OFG gradiometer in which differentiation is taken at sensor head level. Numerical analysis was conducted to demonstrate the system output and determine the optimum values for the system design parameters. The developed experimental system successfully detected a 50 μm steel ball in unshielded environment with signal to noise ratio of 5. The proposed detection system has potential of detecting smaller particles. In addition, the developed particle detection system can also be used for magnetic nanoparticles (MNP) detection for liquid phase Immunoassay applications.

5. References
DRY ETCHING OF GERMANIUM WAVEGUIDES BY USING CHF\textsubscript{3} INDUCTIVELY COUPLED PLASMA

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Abstract: A dry etching procedure to etch germanium in a CHF\textsubscript{3} inductively coupled plasma (ICP) using a polymer based photoresist mask was developed to obtain a high selectivity ratio as well as to obtain a near vertical anisotropic sidewall etch profile. In this study, a sidewall angle of 85° with an etch rate of 190 nm/min was obtained through optimization of the ICP bias power to fabricate germanium waveguide structures with no under-cut.

1. Introduction

The integration of optoelectronics and electronics that are compatible with existing Si based complementary metal-oxide-semiconductor (CMOS) technology is a much highly desired objective. Numerous concepts have been investigated such as in hybrid photon integration of III-V devices and monolithic Si photonic integration. Although hybrid III-V devices integration has made tremendous progress in recent years, there are still difficulties integrating it into the standard CMOS flow such as incompatibility in the fabrication and bonding processes and temperatures. Monolithic Ge-based photonics has been touted as one of the most promising options in order to realize active and passive optical functionalities in Si CMOS-compatible photonic circuitry [1]. Reports have been published concerning the implementation of Ge-based devices showing efficient optical modulation and photo detection within the telecommunication wavelength range and although despite being an indirect bandgap semiconductor, the direct bandgap optical properties of Ge have also been extensively reported for use in active optical devices [1].

Majority of the Ge devices reported however, tend to make use of a oxide or metal hard mask during the fabrication process due to the faster etching rate of a polymeric photoresist mask compared to Ge [2]. Removal of the hard mask can be done through plasma processing. However, exposure to further plasma processing may lead to additional damage to the structures surface and sidewall and can lead to greater loss [3]. In this study, a novel dry etching fabrication process for Ge was developed and optimized using a polymeric mask to produce a selective etching recipe and near vertical sidewall.

2. Experiment

N-type Ge wafers with a (110) crystal orientation were used throughout the development process. Firstly, the wafers were cleaned in warm butanol followed by warm isopropyl alcohol and blow dried in N\textsubscript{2} gas. A polymer based photoresist; 23CP by Tokyo Ohka Kogyo Co. Ltd was used as the photoresist mask and spin coated onto the Ge surface. The samples were then baked on a hotplate at 90°C for 90 seconds. The waveguide structures were defined by lithography technique, developed using a photoresist developer and post exposure baked again on a hot plate at 90°C for 60 seconds before being etched in the ICP for 60 seconds with the same operating conditions (chamber pressure of 1.5x10\textsuperscript{-4} Torr, RF bias power of 50 W, CHF\textsubscript{3} flow rate of 10 sccm), except for the ICP bias power which was varied from 800 W to 1400 W. Finally, the residual photoresist was removed using the photoresist remover and rinsed in warm isopropanol.

3. Results and discussion

Two figures of merit were considered in the fabrication of the Ge waveguide structure. The first figure of merit is the selectivity of the etching ratio between Ge versus the photoresist. This first figure of merit is interwoven with the etch rate for Ge and photoresist. The second figure of merit is that the sidewall angle should be vertical with minimal under etching of the waveguide structure. An overview of the etching process is given in Figure 1.

Fig. 1. Schematic overview of the ICP process, (a) photoresist on Ge (b) CF\textsubscript{3} passivation layer (c) etching process (d) final etch profile and sidewall angle θ definition.

There are two competing phases that occur during the etch process. One is where a passivation layer is deposited onto the photoresist and Ge surface and another is where the photoresist and Ge material is etched. CHF\textsubscript{3} is reported to dissociate into a number of...
different neutral and ionic radicals by electron impact dissociation during the ICP process and as seen in Table 1 [4].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Threshold energy (eV)</th>
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<tbody>
<tr>
<td>CHF₃ + e → CF₂ + HF (1)</td>
<td>2.43</td>
</tr>
<tr>
<td>CHF₃ + e → CF₃ + H (2)</td>
<td>4.52</td>
</tr>
<tr>
<td>CHF₃ + e → CHF₂ + F (3)</td>
<td>4.90</td>
</tr>
<tr>
<td>CF₃ + e → CF₂ + F (4)</td>
<td>3.83</td>
</tr>
<tr>
<td>CF₂ + e → CF + F (5)</td>
<td>5.35</td>
</tr>
</tbody>
</table>

Table 1. Electron impact dissociation of CHF₃ and corresponding threshold energies

As seen in Table 1, the lowest threshold energy is exhibited by the dissociation of CHF₃ into CF₂ gas which is a polymeric precursor. Clustering of CF₂ then subsequently leads to its deposition onto the etching surface as a passivation layer. The passivation layer helps to protect the photoresist and enables greater selectivity.

Using the optimized dry etching conditions, Ge is etched at a rate of 190 nm/min while the photoresist is etched at a rate of 35 nm/min giving a selectivity ratio of 5:1 (Ge: photoresist).

In order to produce a vertical sidewall angle with no under etching, both physical bombarding as well as chemical reactions must be optimized during the etching process. The main components for physical etching are the F radicals produced by the further dissociation of CHF₃ which reacts with Ge to produce GeF₄ gas that can be pumped out from the ICP chamber.

HF has been reported to readily etch Ge [5] and the HF produced by the CHF₃ dissociation provides the chemical reaction component of the etching mechanism.

The vertical angle of the sidewall can be optimized by varying the ICP bias power as shown in Figure 2.

![Fig. 2. SEM images of Ge fabricated with ICP bias power and corresponding sidewall angle θ (a) 800 W (50°) (b) 1000 W (55°) (c) 1200 W (85°) (d) 1400 W (70°).](image)

The sidewall angle increases to near vertical when applying an ICP bias power of 1200 W leading to an optimized equilibrium between the physical and chemical etching components as shown in Figure 3. Below 1200 W of ICP bias power, the sidewall angle is bevelled while at ICP bias power of 1400 W, under etching is evident leading to narrowing of the waveguide structure and a sloping sidewall.

The photoresist mask can then be easily removed after etching using the photoresist remover and cleaned in warm isopropanol.

4. Conclusion

Dry etching conditions to fabricate germanium waveguide using a polymer photoresist mask has been developed and optimized to produce a highly selective etch and near vertical sidewall angle. The results obtained may provide a simpler low damage dry etching procedure for fabrication of germanium waveguides and optical devices.

Acknowledgements

The authors would like to acknowledge Profs. D. Wang and H. Nakashima of Kyushu University for their useful discussion and advice.

References

SUPPRESSING NEW GRAPHENE NUCLEI GENERATION BY HYDROGEN SWEEPING

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Abstract: New graphene nuclei continually appear during CVD process when using Cu as catalyst could be the main issue to get large domain graphene. Here we reported a facile way to suppress new graphene nuclei generation by introducing H2 by interval time. Finally, we found new graphene nuclei could be effectively suppressed by this method.

1. Introduction

Recently, there are many reports about decreasing the graphene density methods when using copper catalyst, such as mild oxidation copper in Argon gas [1-3], copper pre-treatment [4], liquid Copper[5], removing carbon impurities on copper [6, 7], Argon pulse[8] and “Vapour Trapping” structure[9-11]. All of above methods were demonstrated to be useful to suppress the graphene density.

Actually, in order to get millimetre, even centimetre size single graphene domain, at least several hours needed for CVD reaction. However, even people could get much lower graphene density in the beginning, we will show that, there is still high possibility that new graphene domain will appear as reaction time grows. The new appearance graphene domains not only increase the graphene density, but lower or even broken the possibility to grow large graphene single domain, especially when the new graphene domain appeared near the previous existing graphene domain. Thus how to suppress or avoiding new graphene nuclei generation and still maintain graphene density as low as beginning during the graphene growing is extremely significate and crucial to get large enough graphene single crystalline domain. Unfortunately, this is usually neglected in most of papers, which mainly focusing on the graphene density on fixing time. There is paper noticed about this but without any resolution [12]. In this paper, we first show the relationship between the graphene density and reaction time. Then we propose a facile method to suppress new graphene nuclei appear when prolong the reaction time.

2. Main text

Copper mild oxidation in Argon gas (including microscale Oxygen) [1-3] or directly heating in air was verified very helpful to suppress graphene nucleation density [8]. After oxidation and reduction, the Cu atoms of active Cu crystal boundaries rearrange into less active structure, and thus the graphene nucleation density can be well decreased after Cu surface oxidation [13, 14]. Thus before our CVD experiment, we heat our copper at 200°C to oxidize copper surface in air. After pre-oxidation in air, we load Cu foil to our CVD chamber to grow graphene. Before introducing methane to CVD system, we anneal copper in 5% hydrogen that diluted in Argon gas as long as 20 min to remove the copper oxide layer at 1070°C. Then we pump in 2% hydrogen and 15 ppm methane (all diluted in Argon gas) for graphene growth at the same temperature. After reaction, we oxidize the copper again at 200°C for 30s in order to visualize the graphene domain directly [15].

For growth times of 30min (Fig.1a), 60min (Fig.1b), and 90min (Fig.1c), the maximum diagonal distances for the graphene domains are ∼556, ∼1056, and ∼1600 um, respectively. This largely linear time dependence indicates that the growth velocity of the edge is constant and the increase in a linear dimension of a growing crystallite is simply proportional to the diffusion rate of the active carbon which is constant at a fixed temperature [16, 17]. That means the graphene domain diameter is proportional to reaction time. If we assume that the largest graphene domain generates at the beginning we could get single graphene domain occurrence time distribution. Fig 1(d-f) shows that there is always new graphene domain generation during CVD reaction period. If we look into Fig.1d, we could found that more than half of the graphene nucleate in the first 10 min, which means the main graphene nucleation process prefer gathering at the beginning. Nevertheless, new graphene domain still will appear continuously in the following reaction time. That indicate even people could get satisfied graphene density at particular time, there is extremely high possibility that new graphene domain will come out if needing increasing reaction time to make graphene bigger.

The biggest disadvantage is the new occurrence smaller graphene domain may ruin the previous larger single crystalline graphene domain, making it poly-crystallization. The overall growth processes for Cu-based graphene could be divided into three main steps that described in Fig.2a step 1-3. (1) CH4 dissociates and is chemically adsorbed on the Cu surface to form the active carbon species (CH4<4) s, where “s” signifies “surface-adsorbed” to...
distinguish it from a gaseous molecule. The exact nature of the active carbon species has not been well-defined and we used carbon monomers (C) to represent all types of active carbon species in Figure 2a. (2) From recent research, the carbon Cu interaction is weak and the desorption rate of active carbon species is comparable to its mobility on the Cu surface above 870 °C. Under the growth conditions described in this paper, the temperature is 1070 °C, suggesting that the movement of active carbon species on the Cu surface is dominated by diffusion and desorption. (3) When active carbon reaches a critical supersaturation point, graphene domains nucleate. Once the graphene nuclei are formed, most of the active carbon species will be captured and consumed in the growth of graphene, reducing the probability that new graphene nuclei will be formed in the nearby area of the Cu catalyst. Because graphene nuclei won’t take place until the concentration of active carbon species reaches to supersaturation level [20, 21], we could put off or even avoiding new nuclei generation if these far away from the existing graphene domain active carbon atoms could be swept away. Hydrogen had demonstrated to a dual role during graphene synthesis [22]: an activator of the surface bound carbon that is necessary for monolayer growth and an etching reagent that controls the size and morphology of the graphene domains. Thus we could utilize hydrogen to etch the free active carbon atoms away (see Fig.2a step 4). After H2 “sweeping” for short time, CH4 gas will be re-introduced and the previous graphene could regrow. In order to verify above idea, we only shut off CH4 gas for 10 minutes every 30 min interval during graphene synthesis section, only keeping Hydrogen and Argon gas on. Fig.2 b-d shows the SEM images when total reaction time is 60 min, 90 min, and 120 min respectively (excluding hydrogen sweeping time), and hydrogen sweeping time is one, two and three respectively. Fig.2e-g are the corresponding graphene domains occurrence distribution. It is obviously that most of graphene domains only generate at the first 30 min. This means by H2 sweeping, new graphene nuclei is successfully suppressed.

Fig.1

A HIGHLY ACTIVE Ni/ZSM-5 CATALYST FOR DEEP HYDROGENATION OF ARENES

Fig.2

4. Conclusion

In this paper we utilize H2 to etching the redundancy active carbon in Cu surface and successfully suppressed new graphene nuclei generation. This method is easy to complete.

5. References


Abstract: A highly dispersive supported nickel catalyst was in situ prepared by decomposing nickel tetracarbonyl onto ZSM-5 zeolite, respectively. Unexpectedly, amorphous nickel was formed onto ZSM-5. Strong interaction between supported nickel and the support is proved. Catalytic hydrogenations of arenes, i.e., durene, anthracene, phenanthrene and the heavy mixture as by-products derived from methanol-to-gasoline conversion, over the catalysts were examined. Ni/ZSM-5 shows a dramatic activity for deep hydrogenation of arenes and complete saturation of arenes can be achieved over the catalyst.

1. Introduction
Risk of petroleum shortage has been stimulating development of coal to oil technologies, including direct coal liquefaction (DCL) and indirect coal liquefaction (IDCL), but the high concentration of arenes in the liquids from DCL and IDCL confines the application of them as clean fuels [1-3]. For instance, methanol-to-gasoline conversion (MTG) is an important IDCL process, but it normally produces substantial amount of a heavy mixture (HM), which mainly consists of unsaturated species, especially polymethylbenzenes (PMBs). Deep hydrogenation of such arenes, either PMBs or condensed arenes (CAs), has thus been a major technical subject [4,5].

None of the catalytic hydrogenation of arenes, reported so far, has reached full hydrogenation of CAs or PMBs. Conventional methods of catalyst preparation, such as impregnation, co-precipitation, sol-gel, and in situ reduction, were investigated extensively. However, those methods are relatively tedious and neither noble nor non-noble metallic catalysts developed so far could completely hydrogenate CAs and PMBs with high yields. A key to preparation to a highly active catalyst is to perform metals loading and reduction below a threshold temperature for avoiding the decrease in specific surface area of metals. Metal carbonyls (MCs) usually decompose at relatively low temperature into metals directly and are therefore ideal precursors of highly active metal particles, which can be used to catalyst preparation processes much simpler than conventional ones. Supported catalysts were prepared through the decomposition of MCs in 1980s. However, preparation of supported metallic catalysts using MCs was not developed since most MCs volatilize rapidly long before decomposition. In the present work, using nickel tetracarbonyl (NTC) for nickel has successfully developed to in situ prepare supported nickel catalysts for deep hydrogenation of arenes.

2. Main text
NTC was synthesized by reacting active nickel powder with CO under 8.0 MPa at 100 °C in a 100 mL stainless steel and magnetically stirred autoclave. Diethyl ether, ZSM-5 zeolite, and NTC were put into the autoclave. After replacing air inside the autoclave with nitrogen, the mixture in the autoclave was slowly stirred for 1 h at room temperature to sufficiently impregnate NTC into the support. Then the autoclave was heated to 100 °C and kept at the temperature for 1 h with rapid agitation to allow in situ decomposition of NTC over the support. After cooling the autoclave, CO in the autoclave was released followed by subsequent heating and cooling process mentioned above to decompose NTC as exhaustively as possible. Then the reaction mixture was taken out from the autoclave and filtrated under nitrogen protection to obtain the supported catalyst.

Catalysis procedures were carried out as follows: THF (20 mL), catalyst (0.5 g), and substrate (arene 5 mmol or HM 1.0 g) were fed into the autoclave. After replacing air in the autoclave and being pressurized with hydrogen to 5.0 MPa at room temperature, the autoclave was heated to an indicated temperature within 20 min and kept at the temperature for a prescribed period of time followed by cooling the autoclave rapidly. The reaction mixture was taken out from the autoclave and filtrated. The filtrate was analyzed with gas chromatograph/mass spectrometry (GC/MS).

As Fig. 1 displays, a number of spherical metal particles with diameter less than 100 nm adhere to the surface of three supports. In Fig. 2, nickel species are supported onto ZSM-5. The nickel supported onto ZSM-5 does not show as the shape of crystals as the former two, but equably and amorphously disperses onto ZSM-5, which results from the restriction of the inner channels of ZSM-5 and the interaction between nickel and the support. The SAED of Ni/ZSM-5 shows a diffraction pattern of amorphous phase as well.

In order to further confirm the catalytic activity of Ni/ZSM-5 towards PMBs, durene was hydrogenated over Ni/ZSM-5 at different temperatures for 24 h to analyze the conversion of

![Fig. 1. SEM and HREM image of the Ni/ZSM-5.](image)
durene (Fig. 3). The complete conversion is observed during the temperature interval from 120 °C to 180 °C, and a conversion jump, from 15% to 96%, could be observed from 80 °C to 100 °C, which indicates the activation temperature for durene is relatively low due to the high activity of Ni/ZSM-5. Nuclear magnetic resonance was used to ascertain the molecular structure of the hydrogenation product: 1H, δ= 0.838, 0.854; 2H, δ= 1.272, 1.284, 1.333, 1.363 and 3H, δ= 1.598, 1.603, which indicate the protons of methyl, methylene and methyldiene, respectively. Corresponding with the ratio of three kinds of protons in 1,2,4,5-tetramethylcyclohexane, the area integrals of these peaks are respectively 3.08, 1.06 and 1.00.

Anthracene and phenanthrene were hydrogenated over the catalyst for 24 h at 180 °C. The anthracene perhydride almost accounts for the whole compositions of products. Deep hydrogenation of phenanthrene is difficult due to its steric configuration. A high catalytic activity of Ni/ZSM-5 is further certified by perhydrophenanthrene yield of 25.8 mol%, and the yield of two-ring hydrogenation products also reaches 63%. The outstanding catalytic activity of Ni/ZSM-5 is attributed to the following two reasons, the amorphous state of nickel loaded inside ZSM-5 and the strong interaction between nickel and the support. The amorphous dispersion of nickel greatly increases the opportunity of interaction between substrates and the catalyst, meanwhile the synergistic effect between nickel and acidic support creates an electron-deficient surface, which substantially increases the activity of metal-loaded and promotes the π bond cracking of arenes.

As shown in Fig. 4, main components in HM are arenes, especially PMBs. The PMBs are extremely difficult to be saturated; meanwhile the blended arenes would restrain mutual activity to be hydrogenated due to the competitive adsorption over active sites. The extremely high activity of Ni/ZSM-5 for hydrogenation successfully overcomes the difficulties. As Fig. 4 (HHM denotes hydrogenated HM) exhibit, all the arenes in HM were catalytically hydrogenated to saturated species over Ni/ZSM-5 at 180 °C for 20 h.

3. Conclusion
In summary, with adopting nickel tetracarbonyl as precursor, a highly dispersive and dramatically active nickel-loaded catalyst Ni/ZSM-5 for the deep hydrogenation of arenes could be in situ prepared. The nickel supported onto ZSM-5 does not show as the shape of crystal, but equably and amorphously disperses onto ZSM-5. The catalyst distinctly facilitate the complete hydrogenation of condensed arenes and polymethylbenzenes. Heavy by-products derived from MTG are completely saturated as well.

4. References
THE ACCELERATED SOLVENT EXTRACTION OF XINYU COKING COAL AND ITS EXTRACTION MECHANISM

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Abstract: Coking coal from Xinyu of Shanxi Province is extracted under elevated temperature and pressure via Accelerated Solvent and Soxhlet Extraction. Analyzing their GC/MS results, we explore the two extraction methods’ impact on the dissolution behavior of small molecules in coal and investigate the mechanism of the extraction.

1. Introduction
Destroying the hydrogen bonds amid coal molecules, VDW and weak complexing forces, solvent extraction frees the solvable molecules in coal [1]. Traditional methods of extraction under ordinary pressure were time-wasted, solvents-exhausted and tedious but with bad efficiency. The Accelerated Solvent Extraction improves the speed and efficiency of the extraction, and decreases the solvent cost, meanwhile separates the solid from liquid phase because the reduced surface tension of solvent, enhanced infiltration capacity and accelerated equilibrium process are generated from solvent heated and forced. In this article, coking coal from Xinyu of Shanxi Province is extracted under elevated temperature and pressure via Accelerated Solvent and Soxhlet Extraction. Analyzing their GC/MS results, we explore the two extraction methods’ impact on the dissolution behavior of small molecules in coal and investigate the mechanism of the extraction.

2. Main text
Coal sample is coking coal after taken off the minerals, comes from Xinyu Preparation Plant of Shanxi Province. It was then pulverized to around 150 mesh. TABLE I shows the proximate and ultimate analyses of the coal sample.

<table>
<thead>
<tr>
<th>TABLE I THE PROXIMATE, ULTIMATE ANALYSIS OF COAL SAMPLE</th>
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<tbody>
<tr>
<td>Proximate analysis/ w%</td>
</tr>
<tr>
<td>M &lt;sub&gt;ad&lt;/sub&gt;</td>
</tr>
<tr>
<td>0.69</td>
</tr>
<tr>
<td>Ultimate analysis/ w%</td>
</tr>
<tr>
<td>C &lt;sub&gt;ad&lt;/sub&gt;</td>
</tr>
<tr>
<td>89.08</td>
</tr>
</tbody>
</table>

Weigh air dried basis coal sample about 2g. Put it in the soxhlet extractor after parcelled with filter paper. Use 1-propanol solvent to extract it 90 minutes at the boiling point temperature. The extracts were refined by rotary evaporation and analyzed by GC/MS. The residues were washed, suction filtered, dried in turn and analyzed by FTIR. Accelerated solvent extraction: Packed by 450 nm PTFE and filter paper respectively, the samples (2 g) were extracted in a 22 mL extraction pool under the pressure of 80 bar and 100 °C. The extraction was cycled for 2 times after static extraction for 15 min. With referring to the extract, the extraction rates (daf, w%) are calculated as follows: 3.85% for accelerated solvent extraction and 3.41% for Soxhlet extraction, respectively.

As shown in Fig. 1 and 2, there are 37 compound categories detected in the soluble substances via accelerated solvent extraction, including 17 alkanes, 13 aromatics, 3 oxy-compounds and elemental sulfur. There are also 37 compound categories detected in the soluble substances via Soxhlet extraction, including 14 alkanes, 22 compounds containing oxygen or nitrogen, 1 thioether, and no aromatics and sulfides detected in it.

2.1 Alkanes
There are 17 alkanes from C<sub>11</sub> to C<sub>27</sub> in the soluble substances via accelerated solvent extraction and 14 alkanes from C<sub>20</sub> to C<sub>33</sub> in the soluble substances via Soxhlet extraction distributing continuously. Despite similar number of compounds, the two soluble substances belong to two different series obviously due to the different numbers of carbon atoms containing in the compounds. The former belongs to alkanes of low carbon and the second one is defined as high carbon. As one kind of small molecules in coal, n-alkanes exist as three states, free state, micropores and network embedded states [2-4]. As for micropores embedded states, mid- and high-carbon n-alkanes usually embedded into relative large micropores due to their big sizes, and low-carbon n-alkanes usually embedded into relative small micropores. Based on their own permeability, solvents are easy to enter the relative large micropores under ordinary pressure of Soxhlet extraction, whereas the solvents also enter the small micropores under the pressure above 80 bar. The diffusing impetus of soluble substances comes from the concentration gradient, which is provided by the circulation flow of solvent in Soxhlet extraction. As a result, accelerated solvent extraction only improves the rate of solvent penetration, but does not benefit the diffusing rate of soluble substances.

2.2 Aromatics
There are 13 aromatics, including derivatives of benzene, naphthalene and anthracene, in the soluble substances via accelerated solvent extraction, whereas no aromatics are detected in the soluble...
substances via Soxhlet extraction. Aromatics are always embedded in the relative small micropores [5], thus such derivatives are not dissolved via Soxhlet extraction. The mechanism of dissolving benzothiophene series is similar with mentioned above.

2.3 Oxy- and nitrogen-compounds

Three oxy-compounds, including only one ester, are detected in the soluble substances via accelerated solvent extraction. However, there are 22 oxy- or nitrogen-compounds, including 6 acids and 9 esters, detected after Soxhlet extraction. Most of them are long chain aliphatic acids or esters, which are obviously embedded in the relative large micropores.

According to the FTIR spectra in Fig. 3, there is no obvious difference about residues' structure characteristics of functional group of two kinds extraction. The reason is that both the extraction rate are low, which is not enough to affect the functional group distribution of the residues.

3. Conclusion

The extractants from ASE mainly contain materials of molecular weight from 142 to 296, i.e. mid- or high-carbon n-alkanes, aromatics and thiophene series, while the extractants from SE contain materials of molecular weight from 228 to 426, i.e. mid- or high-carbon n-alkanes, and aliphatic hydrocarbons (or esters) of long carbon chains. Because of the limited time, the solvent in SE only enters the relative large micropores. However, the solvent in ASE can enter both relative large and small micropores simultaneously. The advantage of ASE is to improve the permeability and permeation rate of solvents, but it makes little contribution to diffusion rate of solvents. The intrinsic reasons for the different results of the two extraction methods are the different molecular weights of the materials embedded in the two kinds of micropores.

4. References