



Quarterly Letter Report

Growth, Characterization and Device Development in
Monocrystalline Diamond Films

DTIC
ELECTE
OCT 05 1993

D

Supported by the Innovative Science and Technology Office
Strategic Defense Initiative Organization
Office of Naval Research
under Contract #N00014-90-J-1604
for the period March 31, 1993-June 30, 1993

R. F. Davis, J. T. Glass, R. J. Nemanich* and R. J. Trew**
P. K. Baumann, T. P. Humphreys, B. R. Stoner, K. F. Turner,
S. D. Wolter, P. Yang and W. Zhu
North Carolina State University
c/o Materials Science and Engineering Department
*Department of Physics
**Electrical and Computer Engineering
Raleigh, NC 27695

Approved for public release
Distribution

June, 1993

93-23002



93 10 1 109

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget Paperwork Reduction Project (0704-0188), Washington, DC 20503				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE June, 1993		3. REPORT TYPE AND DATES COVERED Quarterly Letter 4/1/93-6/30/93
4. TITLE AND SUBTITLE Growth, Characterization and Device Development in Monocrystalline Diamond Films			5. FUNDING NUMBERS s400003srr08 1114SS N00179 N66005 4B855	
6. AUTHOR(S) Robert F. Davis				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) North Carolina State University Hillsborough Street Raleigh, NC 27695			8. PERFORMING ORGANIZATION REPORT NUMBER N00014-90-J-1604	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Sponsoring: ONR, Code 1513:CMB, 800 N. Quincy, Arlington, VA 22217-5000 Monitoring: Office of Naval Research Resider The Ohio State University Research Center 1960 Kenny Road Columbus, OH 43210-1063			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) A series of computer-based statistical experimental designs have been conducted to determine the optimum conditions for negative bias-enhanced nucleation of diamond. The concentration of CH ₄ and the effects of pressure and bias voltage on the time for complete coverage of the substrate, film uniformity and nucleation density were the experimental parameters and desired results investigated. Time to complete film formation, uniformity and nucleation density were all improved with the use of both a negative bias voltage and high CH ₄ concentrations. Diamond has also been formed on diamond seeds placed on nickel substrates via microwave plasma CVD. The long range nucleation density was low and the formation of clusters of diamond more common. Polycrystalline Si-Ge films have been grown by e ⁻ beam deposition on naturally occurring p-type semiconducting diamond C(001) substrates. Room temperature and 300°C I-V data show the formation of a low-barrier rectifying contacts which exhibit ohmic behavior. Annealing at 850°C under UHV conditions resulted in apparent degradation in the I-V characteristics.				
14. SUBJECT TERMS diamond, statistical design, deposition experiments, bias enhanced nucleation, nucleation density, Si-Ge ohmic contacts			15. NUMBER OF PAGES 24	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLAS	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLAS	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLAS	20. LIMITATION OF ABSTRACT SAR	

Table of Contents

I.	Introduction	1
II.	Investigation of Process Parameter and Substrate Effect of Bias-enhanced Nucleation	3
III.	Microwave Plasma Chemical Vapor Deposition of Diamond on Nickel	11
IV.	Growth and Characterization of SiGe Contacts on Semiconducting Diamond Substrates	17
V.	Distribution List	24

Accession For		
NTIS	GRAB	☒
DTIC	TAB	☐
Unannounced		☐
Justification		
By		
Distribution/		
Availability Codes		
Dist	Avail and/or Special	
A-1		

DTIC QUALITY INSPECTED 2

I. Introduction

Diamond as a semiconductor in high-frequency, high-power transistors has unique advantages and disadvantages. Two advantages of diamond over other semiconductors used for these devices are its high thermal conductivity and high electric-field breakdown. The high thermal conductivity allows for higher power dissipation over similar devices made in Si or GaAs, and the higher electric field breakdown makes possible the production of substantially higher power, higher frequency devices than can be made with other commonly used semiconductors.

In general, the use of bulk crystals severely limits the potential semiconductor applications of diamond. Among several problems typical for this approach are the difficulty of doping the bulk crystals, device integration problems, high cost and low area of such substrates. In principal, these problems can be alleviated via the availability of chemically vapor deposited (CVD) diamond films. Recent studies have shown that CVD diamond films have thermally activated conductivity with activation energies similar to crystalline diamonds with comparable doping levels. Acceptor doping via the gas phase is also possible during activated CVD growth by the addition of diborane to the primary gas stream.

The recently developed activated CVD methods have made feasible the growth of polycrystalline diamond thin films on many non-diamond substrates and the growth of single crystal thin films on diamond substrates. More specifically, single crystal epitaxial films have been grown on the {100} faces of natural and high pressure/high temperature synthetic crystals. Crystallographic perfection of these homoepitaxial films is comparable to that of natural diamond crystals. However, routes to the achievement of rapid nucleation on foreign substrates and heteroepitaxy on one or more of these substrates has proven more difficult to achieve. This area of study has been a principal focus of the research of this contract.

At present, the feasibility of diamond electronics has been demonstrated with several simple experimental devices, while the development of a true diamond-based semiconductor materials technology has several barriers which a host of investigators are struggling to surmount. It is in this latter regime of investigation that the research described in this report has and continues to address.

In this reporting period, the optimum process parameters for bias-enhanced nucleation including methane concentration and the effects of total pressure and bias voltage have been investigated using a computer-based statistical package. The growth of diamond films on diamond-seeded Ni surfaces has also been investigated in a microwave plasma. Finally, ohmic contacts to p-type diamond have been produced from Si/Ge films deposited by electron beam evaporation.

The following subsections detail the experimental procedures for each of the aforementioned studies, discuss the results and provide conclusions and references for these studies. Note that each major section is self-contained with its own figures, tables and references.

II. Investigation of Process Parameter and Substrate Effect of Bias-enhanced Nucleation

A. Introduction

Bias-enhanced nucleation (BEN) of diamond has resulted in higher than typical nucleation densities as compared to the conventional scratching or seeding methods. This technique involves a negative substrate bias to promote nucleation. Since diamond has an extreme surface energy, a film of diamond may be obtained via BEN in a short time span by relying on an enhanced number of nuclei rather than two-dimensional growth. Also, no deleterious surface preparation is required to form the stable diamond nuclei during this process, which may have been one factor for the epitaxial deposition of diamond observed on β -SiC.[1]

The initial studies conducted by Yugo *et al.*[2, 3] observed the effect of substrate biasing on the nucleation density. Stoner *et al.*[4] utilized *in-vacuo* characterization of this process to better understand the surface and near-surface effects of the negative bias.

This study pertains to the investigation of the process parameters utilized during BEN. A series of "statistical experiment designs" were conducted involving two different CH_4 concentrations and the effects of pressure and voltage on: (i) time for a complete film to form, (ii) film uniformity, and (iii) nucleation density. Various substrates were also investigated in comparison to the silicon results.

B. Experimental Procedures

Parametric Study of Bias-enhanced Nucleation. This research was conducted in a microwave plasma chemical vapor deposition chamber.[4] Silicon substrates were used as-received from Virginia Semiconductor, Inc. These substrates were mirror polished single-side only and cleaned using an RCA cleaning technique. The substrates were rinsed in de-ionized water just before entering into the growth chamber.

The primary process parameters which influence the BEN (i.e., pressure, methane concentration and bias voltage) were investigated using a statistical experimental design (SED). BEN has been utilized to promote nucleation and the biasing set-up utilized in this study has been previously discussed.[2-5] Laser reflection interferometry (LRI) was used to monitor the time at which a film of diamond was obtained.[5] Scanning electron microscopy (SEM) was used to determine the nucleation density as well as the film uniformity. Though the film uniformity is important to determine, it may vary depending on the set-up of the growth system.

Substrate Influence during Bias-enhanced Nucleation. Various substrates were investigated to observe the influence of biasing on the nucleation density. The influence on the nucleation density has been the fundamental measuring rod for determining the success of BEN. The

attainment of a very high nucleation density on silicon without scratching or seeding ultimately was the motivation for attempting this pretreatment technique on Si.

Titanium, niobium, tantalum, and tungsten were chosen because of their carbide forming nature and germanium was chosen for comparison. The samples were polycrystalline and polished down to $0.05\mu\text{m Al}_2\text{O}_3$ to eliminate the possibility of diamond seeding during the preceding polishing steps. The samples were then cleaned in trichloroethylene, acetone, methanol, and 2-propanol and thoroughly rinsed in de-ionized water prior to entering into the growth chamber. SEM was used to determine the nucleation density on these materials.

Stoner *et al.*[6] reported the necessity of diamond on the substrate holder during BEN. With no such coating there was no enhancement in the diamond nucleation density. Therefore, for both the parametric study, as well as the BEN study involving the various substrate materials, care was taken to ensure that a suitable quantity of diamond was coated on the substrate holder.

C. Results and Discussion

Parametric Study of Bias-enhanced Nucleation. Silicon has been proven to be an effective substrate for BEN. Not only has there been a large influence on the nucleation density, but epitaxial diamond particles have been obtained.[1] The graphics in Figs. 1, 2, and 3 detail the influence of pressure, methane concentration, and bias voltage on three areas of interest in this study. These are the time to a continuous film of diamond, nucleation density, and film uniformity, respectively. These figures reveal that a bias voltage of -300 to -350 VDC, a pressure of roughly 20 torr, and a methane concentration of 15% are ideal for satisfying these three criteria. Thus, these region is referred to as a sweet spot.

As discussed in the experimental section, Fig. 4 signifies the necessity of diamond on the substrate holder during BEN. As this plot indicates, with an adequate amount of diamond on the substrate holder, a consistent time to form a film of diamond is attained. It should also be noted that as more diamond is grown on the substrate holder the bias current is increased. This is speculated to be due to the emission of electrons from the substrate holder diamond.[6] Either the emitted electrons or diamond particulate migration to the substrate are proposed as mechanisms responsible for diamond nucleation during BEN.[6].

Substrate Influence during Bias-enhanced Nucleation. In a previous study, copper was proven to be a much less effective substrate, introducing a possible substrate effect of BEN. In this regard BEN has been attempted on various refractory materials since the influence of BEN may be linked to the carbide forming nature of the substrate. In Fig. 5 the plot indicates that the carbide forming substrates do show more of an influence for establishing an enhanced number of diamond as compared to the non-carbide forming germanium and copper substrates. Silicon

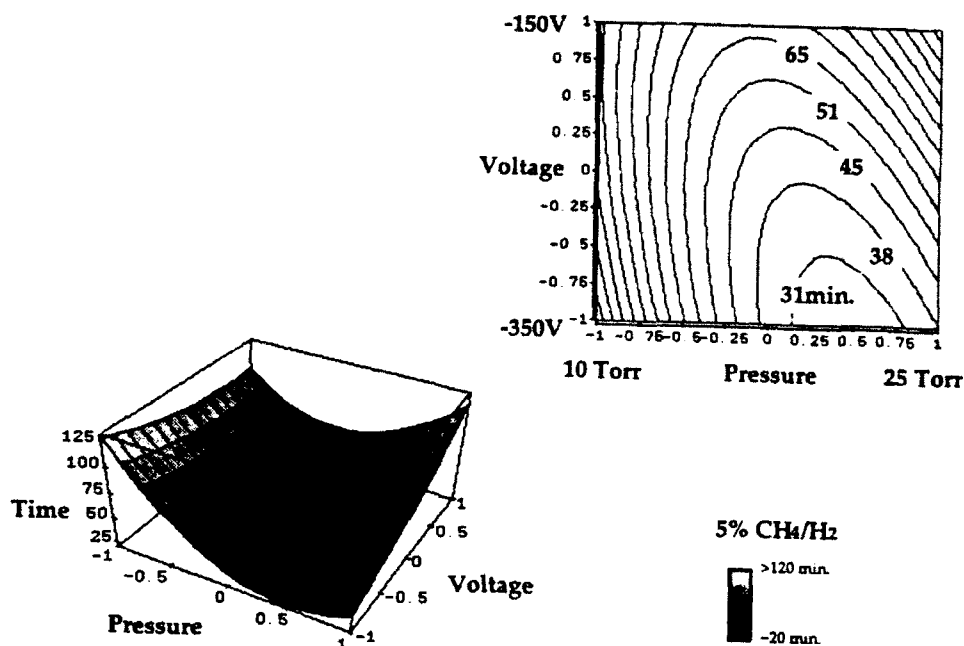


Figure 1a. Time for a complete film of diamond to form - 5% CH_4/H_2 .

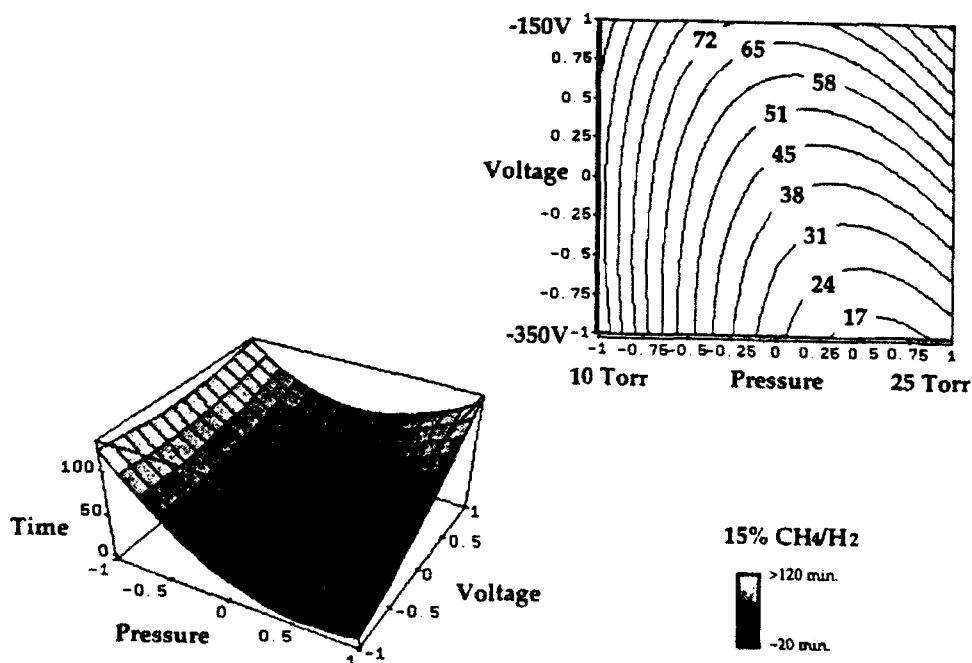


Figure 1b. Time for a complete film of diamond to form - 15% CH_4/H_2 .

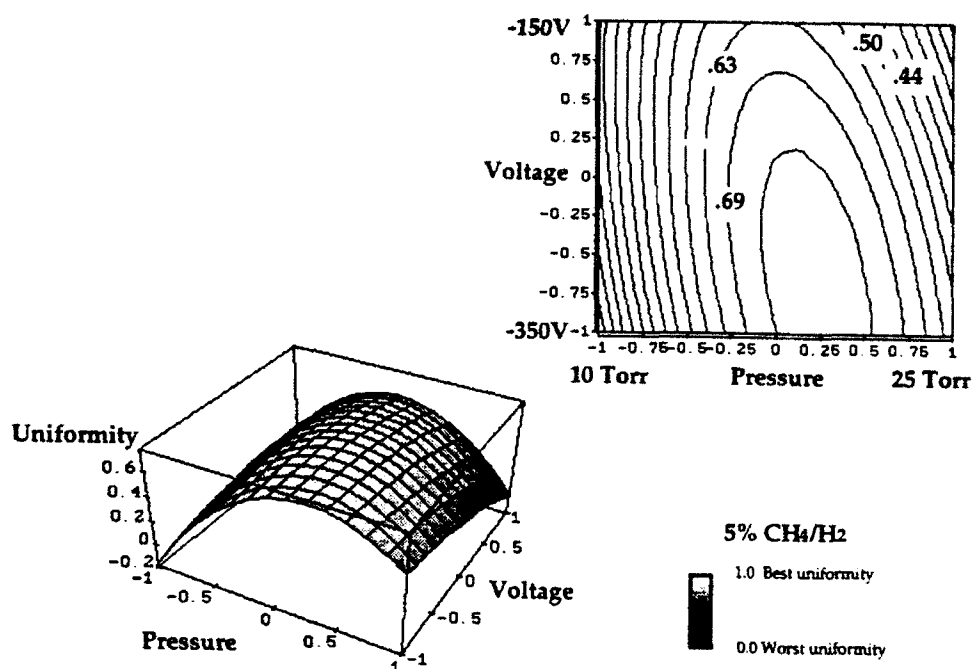


Figure 2a. Diamond film uniformity - 5% CH_4/H_2 .

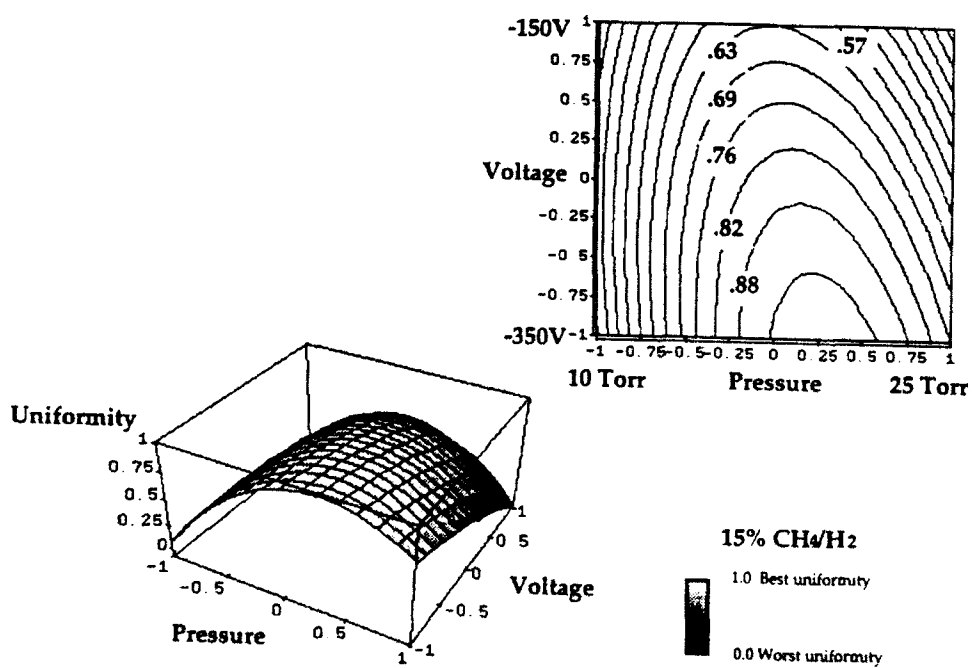


Figure 2b. Diamond film uniformity - 15% CH_4/H_2 .

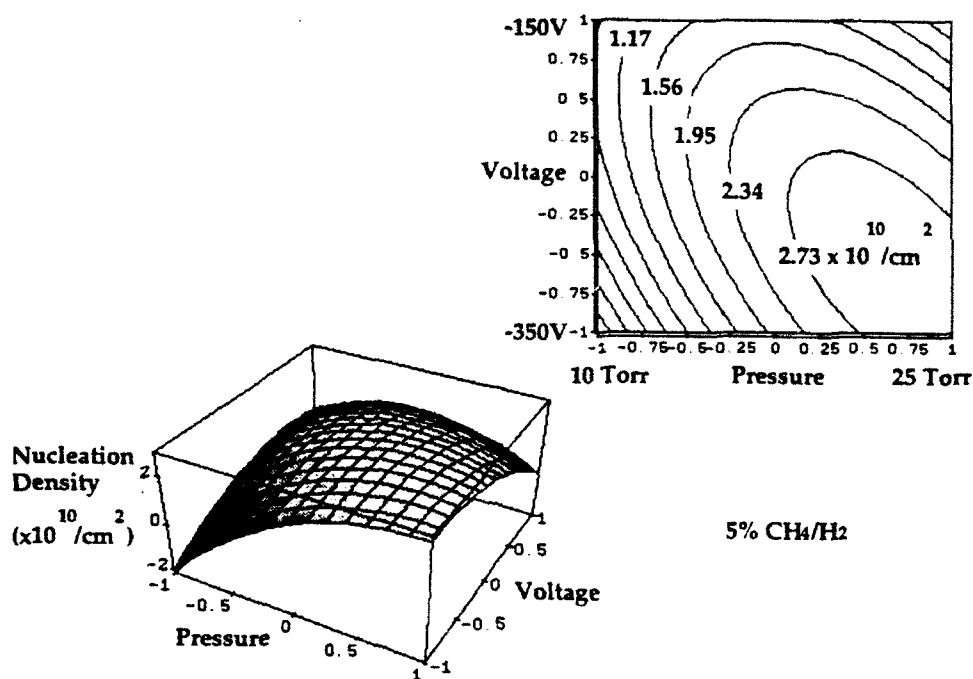


Figure 3a. Diamond nucleation density - 5% CH_4/H_2 .

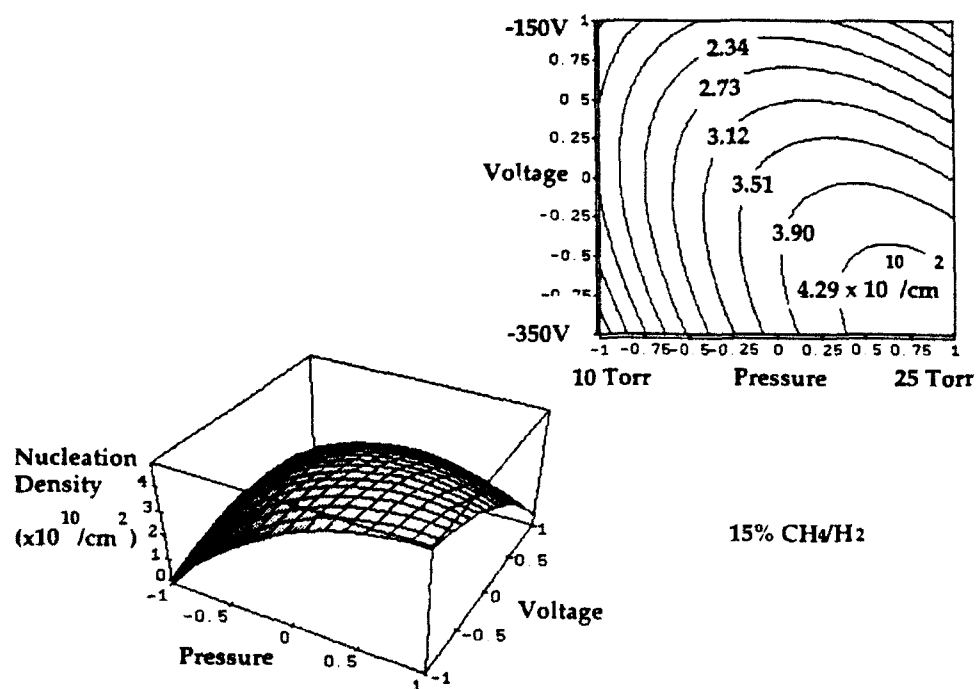


Figure 3b. Diamond nucleation density - 15% CH_4/H_2 .

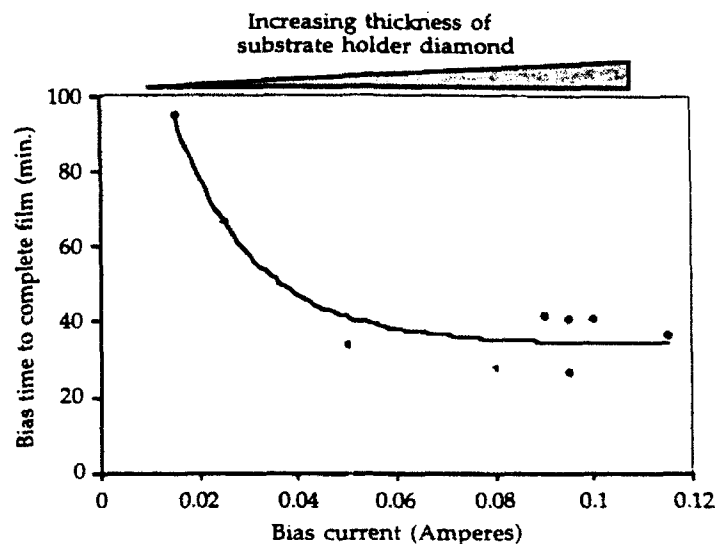


Figure 4. Relative importance of substrate holder diamond for obtaining diamond nucleation as well as acquiring consistent results.

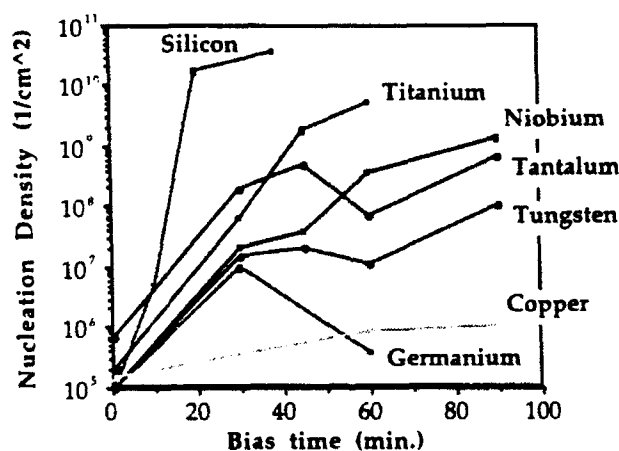


Figure 5. The plot indicates that the carbide formers were more influenced by the negative substrate bias. Among these carbide formers silicon was more successful for forming a high density of nuclei in a short time span as compared to the refractory substrates.

is the most effective substrate indicating a property (or properties) of this material which enables it to provide sites onto which diamond may nucleate. The refractory substrates typically form carbides exhibiting the rock salt structure, excluding tungsten carbide which is hexagonal. The heat of formation of the refractory carbides in addition to the activation energy for diffusion of carbon in these materials is plotted in Fig. 6 along with the nucleation density at 60 minutes of biasing. These material properties of the refractory substrates show some

correlation as this plot indicates. However, the silicon substrates do not follow the same trend that was observed for the refractory substrates. This indicates a property (or properties) unique to silicon that results in an extreme influence of BEN. Further study is required to understand this result in more detail.

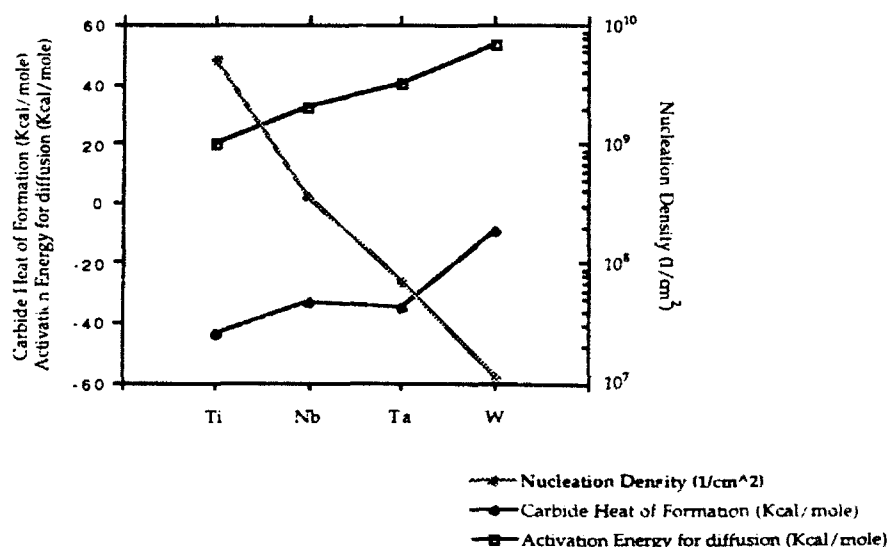


Figure 6. The materials properties shown below were plotted along with the nucleation density for the refractory substrates. A correlation of this data was observed and may provide insight into what mechanisms are responsible for nucleation as well as seeking an alternative substrate to that of silicon.

D. Conclusion

The process parameters utilized during bias-enhanced nucleation were investigated to reveal the parametric space for highest nucleation density, shortest time of biasing to form a complete film of diamond, and optimum film uniformity. These process parameters were pressure, methane concentration, and bias voltage. A bias voltage of -300 to -350 VDC, a pressure of roughly 20 Torr, and a methane concentration of 15% were found to be ideal. Intensifying the bias voltage beyond -350 VDC resulted in etching of the diamond both on the substrate holder as well as the substrate.

The refractory substrates were found to be more influenced by BEN as compared to the non-carbide forming germanium and copper substrates. It was speculated that the carbide forming nature of silicon may be a key ingredient for its success during BEN. Thus, this was the motivation behind studying the influence of BEN on these refractory materials. Though the refractory substrates did not surpass the success of silicon there was a correlation between the heat of formation of the refractory carbide and the activation energy for diffusion of carbon in

the refractory material and that of the nucleation density of the refractories after 60 minutes of biasing.

E. Future Research

Future research will attempt to more fully understand the mechanism of biasing and improve the heteroepitaxial growth of diamond. Buffer layers of various types will be employed to improve lattice matching and interfacial strain. Also, Ni samples will be utilized as substrates in a manner similar to recent work in the hot filament deposition of diamond in order to improve misorientations in the resulting films. This is believed to enable the elimination of low angle grain boundaries.

F. References

1. B. R. Stoner and J. T. Glass, Appl. Phys. Lett., **60** (1992) 698-700.
2. S. Yugo, T. Kanai, T. Kimura and T. Muto, Appl. Phys. Lett., **58** (1991) 1036-8.
3. S. Yugo, T. Kanai, T. Kimura and A. Ono, 1990, p. 944-947.
4. B. R. Stoner, G.-H. M. Ma, S. D. Wolter and J. T. Glass, Phys. Rev. B, **45** (1991) 11067-11084.
5. B. R. Stoner, B. E. Williams, S. D. Wolter, K. Nishimura and J. T. Glass, J. Mater. Res., **7** (1991) 1-4.
6. B. R. Stoner, G. H. Ma, S. D. Wolter, W. Zhu, Y.-C. Wang, R. F. Davis and J. T. Glass, *Diamond and Related Materials* **2** (1993) 142-146.

III. Microwave Plasma Chemical Vapor Deposition of Diamond on Nickel

A. Introduction

It has been well documented that diamond may be formed under high temperature and high pressure (HPHT) conditions utilizing nickel as a catalyst [1,2]. Also, diamond may be formed at reduced pressures in which graphite is the most stable form of carbon. The low pressure synthesis of diamond has been targeted for microelectronic application since it reduces the opportunity for impurity incorporation. The use of nickel in this growth regime typically results in the formation of graphite rather than diamond. Sato *et al.* [3] have indicated that it is possible under certain conditions to form diamond on nickel at low pressure but the dramatic catalytic effects under which diamond is formed at high temperature and high pressure are not displayed. There has been recent success in not only forming diamond on nickel but also obtaining highly oriented diamond [4–6]. This has been readily obtained on both Ni(100) and Ni(111) surfaces and does not show a preference for the ease at which the oriented particles are attained with respect to the substrate surface orientation. The mechanism(s) responsible for the formation of diamond rather than graphite (in appreciable amounts) as well as the attainment of oriented diamond is not fully understood but there have been speculations for these possible mechanisms [6]. Future studies utilizing surface analysis may assist in understanding this phenomenon.

This study involves diamond formation on nickel substrates performed in a microwave plasma chemical vapor deposition (CVD) chamber, in contrast to the recent work performed in a hot filament CVD chamber [4–6]. Laser reflection interferometry (LRI) has been utilized to investigate the possible dissolution of carbon on the nickel surface as well as any other surface changes during the various stages of deposition.

B. Experimental Procedure

Various procedures were undertaken to assure very little graphite formation in addition to obtaining oriented diamond particles. The full understanding of the relative importance of each of these procedures, to be discussed shortly, is still under investigation. But it is to be noted that each procedure or step was performed *in vacuo* in the microwave plasma CVD chamber. This chamber and the LRI set-up have been discussed previously [8]. The nickel was polycrystalline and highly polished using 0.1 μm diamond grit. The substrates were solvent cleaned using a typical cleaning procedure employed in our laboratory of trichloroethylene, acetone, methanol, and 2-propanol. The substrates were then thoroughly rinsed in de-ionized water. Following the cleaning procedure these substrate were seeded using 1.0 μm diamond

that was suspended in acetone. A notable haze was observed on these substrates following this procedure. The samples were then entered into the growth chamber.

A three-step process was used which was similar to the steps used in the hot filament system. Table I lists the conditions under which each step was performed. The first and second steps were responsible for deterring graphite formation and providing a surface on which oriented diamond may form. The diamond seeds are either etched away or dissolved in the nickel matrix during these steps. The third step has merit with respect to providing conditions for which diamond will grow and graphite will be deterred, however, there is no indication that this step is relevant to the formation of oriented diamond particles.

Laser reflection interferometry was used as an in situ monitor of the nickel surface during the three-step procedure. Scanning electron microscopy and Raman was used to investigate the macroscopic and microscopic quality of the diamond formed on the nickel.

Table I.

Parameters	Step 1	Step 2	Step 3
CH ₄ /H ₂	0%	0%	0.4%
Pressure	25 Torr	25 Torr	25 Torr
Power	900 Watts	1200 Watts	900 Watts
Plasma position	Remote	Immersed	Remote
Temperature	900°C	1050°C	900°C
Time	1 hr.	15 min.	Extended

C. Results and Discussion

Figures 1a and b show typical diamond particles employed in this study. The Raman performed indicates good quality diamond (Fig. 2). A noted attribute of this study was the relatively low nucleation density. The diamond that formed did so in clusters. It also appears that some degree of orientation of the diamond particles may have occurred as is evidenced in the micrographs of Fig. 1. Attempts were taken to enhance the nucleation density but altering a few of the process parameters appeared to have little effect. A considerable amount of time was spent investigating the relevance of the second step, since this step is believed to be important for affecting both the nucleation density and the observation of the oriented diamond particles. In the present study the authors found that extending the time at this high temperature step resulted in an extremely low diamond nucleation density and very little graphite. Likewise, a

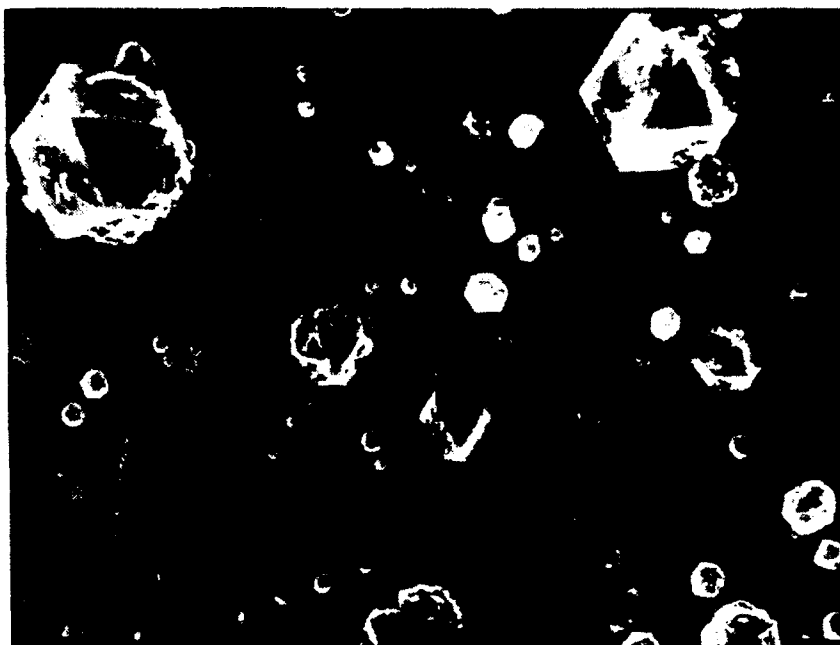


Figure 1a. Diamond particles on polycrystalline nickel- low magnification.



Figure 1b. Diamond particles on polycrystalline nickel- high magnification.

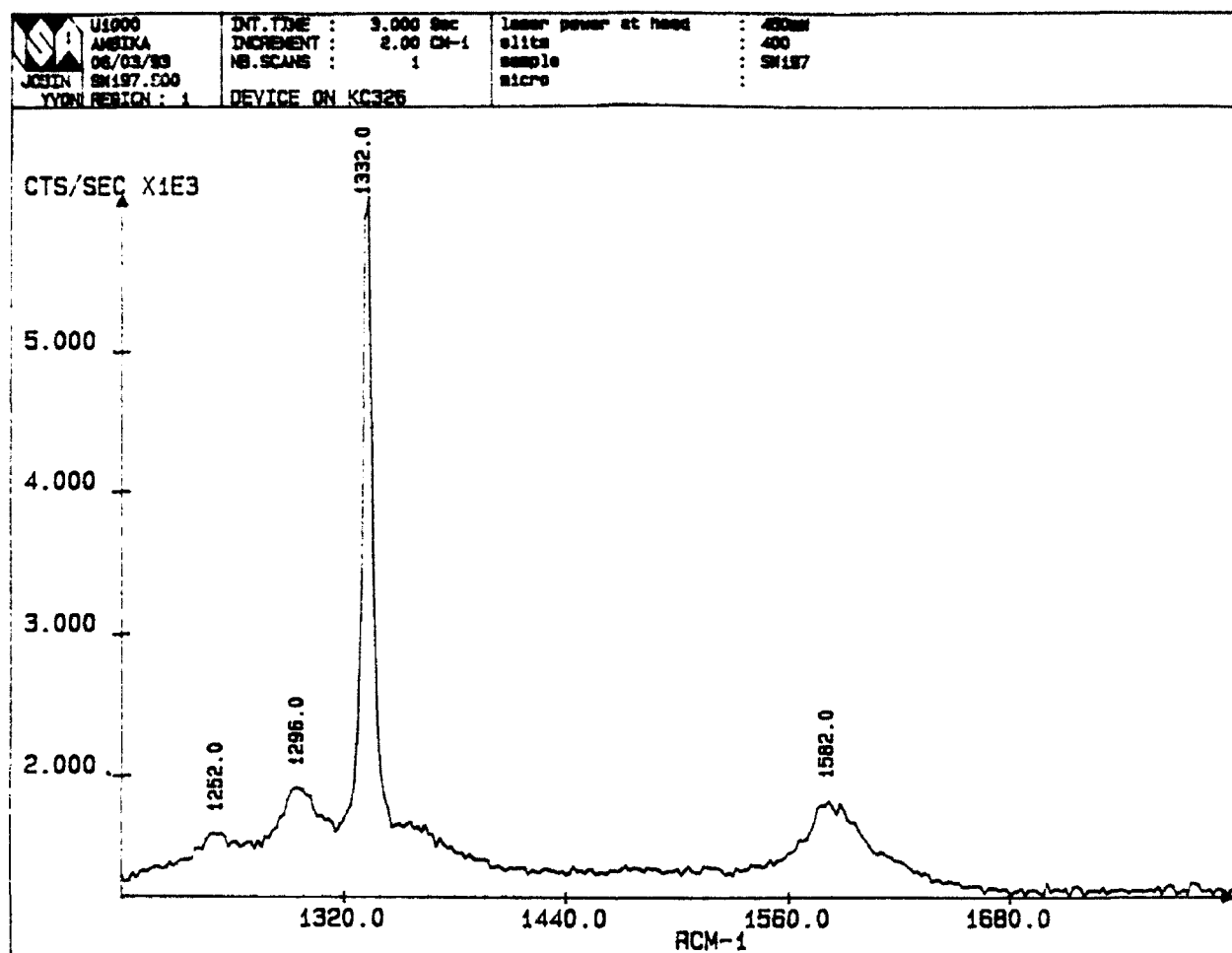


Figure 2. Raman spectra of diamond formed on nickel.

short time at this temperature resulted in the formation of graphite. It is speculated that further dissolution of carbon following the first step is imperative for deterring graphite formation. The nickel surface at this point has been suggested to have formed a ternary phase involving nickel, carbon, and hydrogen. Either the dissolution of carbon or the absorption of hydrogen may not have been adequate at this short time during the second step.

The LRI scan in Fig. 3 shows that the diamond seeds are dissolved or etched quite early. A constant reflectivity is obtained in approximately 15 minutes and by visual inspection this surface appears shiny as opposed to the hazy surface observed following the seeding procedure. The increase in surface reflectivity during the second step may be due to an increased glow of the substrate holder at the elevated temperature. The decrease in intensity of the LRI scan after this high temperature step was due to reduction in substrate temperature. The temperature was reduced to 900°C before the methane was introduced. Immediately after introducing the methane into the chamber during the third step a dramatic reduction in the

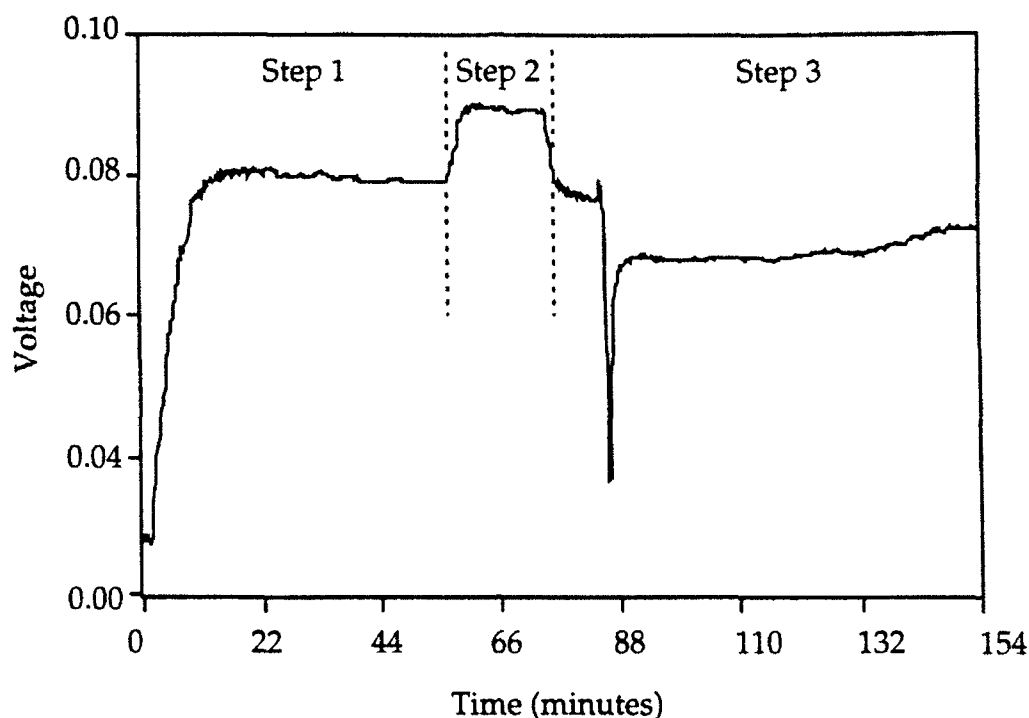


Figure 3. Laser reflection interferometry of the three-step process.

reflectivity is noted. Shortly after, the surface reflectivity increases close to its original reflectivity. This may be due to an initial adsorption of carbon via the methane to the surface.

D. Summary

Diamond has been formed on nickel substrates via microwave plasma chemical vapor deposition. The diamond particles appear to have a preferred orientation as viewed in the individual grains of the polycrystalline substrates. The long range nucleation density is low and the formation of clusters of diamond was more common. The LRI data has shown an immediate dissolution or etching of the diamond seeds from the nickel surface which may have importance for the formation of diamond rather than graphite as well as the formation of oriented diamond.

E. Acknowledgment

The authors wish to thank Ms. A. Somashekhar and Professor R. Nemanich for performing the Raman Spectroscopy in this study. The financial support of this research was provided in part by SDIO/IST through ONR and the Kobe Steel, Ltd. Professorship at NCSU.

F. References

1. H. M. Strong, *Acta Metallurgica* **12**, 1411 (1964).
2. R. H. Wentorf and Jr., *Adv. Chem. Phys.* **9**, 365 (1965).

3. Y. Sato, I. Yashima, H. Fujita, T. Ando and M. Kamo, in: *Mat. Res. Soc. Int. Conf. Proc. on New Diamond Science and Technology*, edited by R. Messier, J. T. Glass, J. E. Butler and R. Roy, Materials Research Society, Pittsburgh, PA, (1991), pp. 371.
4. P. C. Yang, W. Zhu and J. T. Glass, *J. Mater. Res.* (1993) (in press).
5. W. Zhu, P. C. Yang and J. T. Glass, *Appl. Phys. Lett.* (1993) (submitted).
6. W. Zhu, P. C. Yang and J. T. Glass, *Proc. of the 2nd International Conference on Applications of Diamond Films*, Tokyo, Japan, Aug. 1993.
7. B. R. Stoner, G.-H. M. Ma, S. D. Wolter, and J. T. Glass, *Phys. Rev. B* **45**, 11067 (1992).

IV. Growth and Characterization of SiGe Contacts on Semiconducting Diamond Substrates*

T. P. Humphreys, P. K. Baumann, K. F. Turner and R. J. Nemanich
Department of Physics, North Carolina State University, Raleigh, North Carolina
27695-8202 USA

R. G. Alley, D. P. Malta and J. B. Posthill
Research Triangle Institute, Research Triangle Park, North Carolina 27709-2194 USA

Abstract

Silicon-germanium films have been grown by electron-beam deposition on naturally occurring p-type semiconducting diamond C(001) substrates. As evidenced by low-energy electron diffraction and scanning tunneling microscopy the SiGe layers are polycrystalline. Corresponding current-voltage (I-V) measurements conducted at room temperature have demonstrated the formation of a low-barrier rectifying contact. Consistent with the observed low-barrier height, the I-V measurements recorded at 300 °C exhibit ohmic-behavior. In addition, subsequent post-growth annealing of the SiGe contacts at 850 °C in ultra-high vacuum has shown an apparent degradation in the I-V characteristics.

*Accepted for publication in the *Proceedings of the 3rd International Conference Symposium on Diamond Materials*, Honolulu, Hawaii, May, 1993

A. Introduction

At present, there is a significant scientific and technological interest in the fabrication of stable ohmic and high-temperature rectifying contacts on diamond [1, 2]. To date, several metals, [3, 4] refractory metal silicides [5] and semiconductors [6] have been investigated as appropriate contact materials to semiconducting single crystal diamond substrates. In particular, the authors have demonstrated that the deposition of heteroepitaxial films of Ni on diamond exhibit excellent high-temperature rectifying properties [4]. Indeed, similar studies conducted on post-growth annealed TiSi_2 contacts on diamond have also shown rectification at high-temperature [5]. Moreover, it has also been recently demonstrated by Venkatesan *et al.* [6] that highly doped polycrystalline Si contacts fabricated on semiconducting diamond substrates form stable high-temperature rectifying diodes. In particular, the Si/diamond heterostructure also affords the potential of fabricating novel heterojunction devices which can be integrated with existing Si-based processing technologies.

In the present study we report initial results pertaining to the growth and characterization of SiGe contacts deposited on natural p-type semiconducting diamond C(001) substrates.

B. Experimental Procedure

Commercially supplied (D. Drucker & ZN.N.V) low-resistivity ($\sim 10^4 \Omega \cdot \text{cm}$, p-type) semiconducting natural diamond (surface orientation (001)) substrates were chemically cleaned. The cleaning procedure included boiling $\text{CrO}_3 + \text{H}_2\text{SO}_4$ (heated to 200°C) for 10 min followed by immersion in aqua regia ($3\text{HCl} + 1\text{HNO}_3$) and standard RCA cleaning solutions. Following cleaning, the samples were mounted on a Mo sample holder and transferred into the electron-beam evaporation chamber. The base pressure in the system was typically 2×10^{-10} Torr. Prior to deposition, the substrates were heated to 550°C for 5 minutes to thermally desorb both water vapor and possibly physisorbed gas contaminants. On cooling to room temperature an unreconstructed (1×1) low-energy electron diffraction (LEED) pattern was observed from the C(001) surface. The substrate temperature was maintained at 550°C and the SiGe films were grown by the co-deposition of Si and Ge using electron beam evaporation. The corresponding Si and Ge fluxes were calibrated to obtain SiGe layers with a 5% Ge composition. By employing a stainless steel shadow mask several SiGe dots of ~ 200 nm in thickness and $3 \times 10^{-3} \text{ cm}^2$ in area were fabricated. Subsequent post-growth *in-situ* annealing of the samples was performed at a temperature of 850°C at 10^{-8} Torr for 30 min.

C. Results and Discussion

Examination of the as-grown films by LEED failed to obtain an ordered surface structure. Indeed, an inspection of the SiGe films by *ex-situ* scanning tunneling microscopy (STM)

showed a highly textured surface morphology which indicated that the deposited layers were polycrystalline, as shown in Fig. 1. The STM image was obtained in the constant current mode with a tip bias of 2 V. The presence of small polycrystalline grains of ~ 100 nm is clearly evident. The corresponding rms surface roughness of the deposited layer has been determined to be ~ 5 nm. Also, it was apparent that the SiGe films exhibit excellent adhesion properties with the underlying diamond substrate. In contrast, STM images of the annealed films were much more difficult to obtain due to their higher resistivity. As shown in Fig. 2, the surface morphology of the annealed films was significantly smoother with a corresponding rms surface roughness of ~ 3 nm and an apparent increase in grain size.

Shown in Fig. 3 is the Raman spectrum of the SiGe films obtained at room temperature using an Ar^+ ion laser (514.5 nm) excitation source. Clearly observed are two distinct phonon peaks pertaining to Si and Ge at 518 cm^{-1} and 300 cm^{-1} , respectively. It is interesting to note that the corresponding SiGe phonon mode, indicative of alloy formation (near 400 cm^{-1}) was not observed. The absence of the SiGe phonon mode would tend to suggest an apparent segregation and clustering of Si and Ge during growth. Differences in the Si and Ge surface mobilities and/or surface energies on the chemically cleaned diamond C(001) surface during the initial stages of growth may account for this behavior [7]. Further studies are currently in progress to study this growth phenomena. Following the high-temperature ultra-high vacuum annealing step only the Si phonon peak was observed in the Raman spectrum. The absence of the Ge phonon mode in the layer was attributed to the evaporation of Ge during thermal annealing.

Current-voltage (I-V) measurements were obtained by mounting the diamond substrates on a Cu plate using Ag paint to form a large area back contact and applying a bias to the SiGe contact using a W probe. The room temperature I-V characteristics obtained for the as-deposited SiGe contacts on semiconducting diamond substrates are shown in Fig. 4. The rectifying character of the SiGe contact is clearly evident. From the I-V measurements a small forward bias turn-on voltage of ~ 0.6 V was estimated. The corresponding reverse bias leakage current density was measured to be $\sim 1.56 \times 10^{-6}\text{ A/cm}^2$ at 20 V. Moreover, from the apparent linear region of the semilogarithmic plot of the forward characteristics an ideality factor n of 2.5 was calculated. This high n value may be an indication that the current conduction at the SiGe/diamond interface is not governed by a thermionic emission mechanism.

It is interesting to note that similar observations have also been reported for Ni, TiSi_2 and Si contacts on semiconducting diamond C(001) substrates (4-6). In each of these studies current conduction appeared to be dominated by a space charge limited current (SCLC) mechanism. Consistent with the small turn-on voltage and the relatively high reverse leakage current, the corresponding I-V measurements recorded at 300°C exhibit ohmic-like behavior.

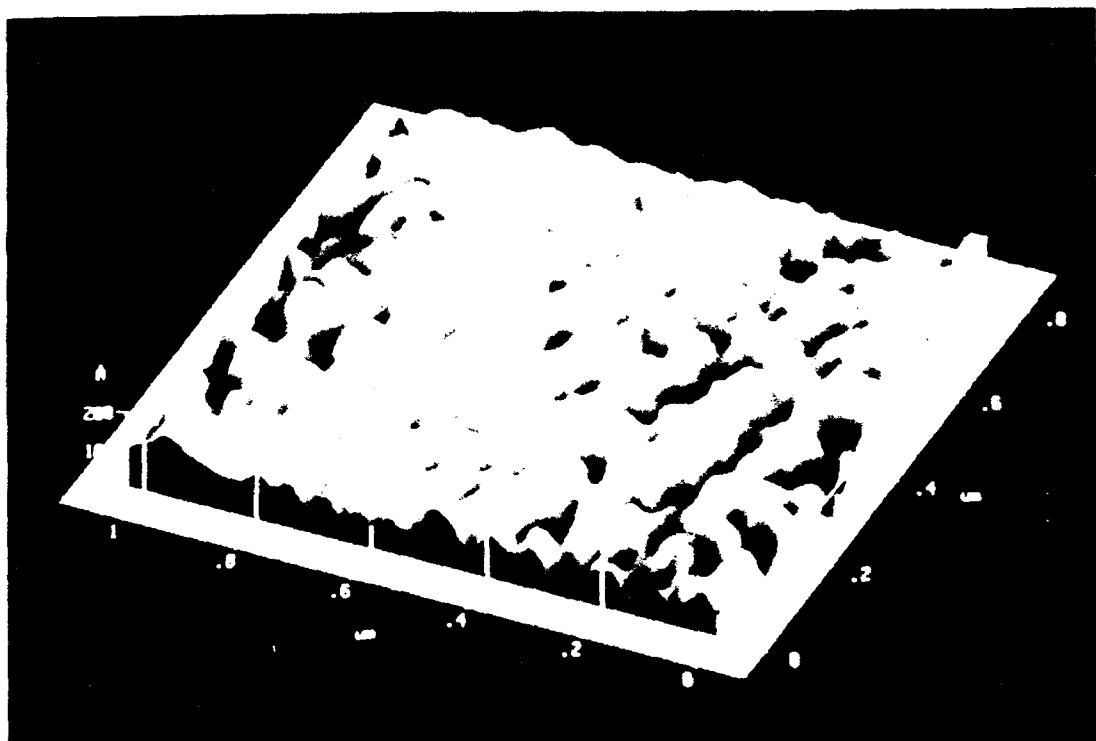


Fig. 1 Topographic (constant current) STM micrograph of the surface morphology of the SiGe film deposited on natural diamond C(001) substrates.

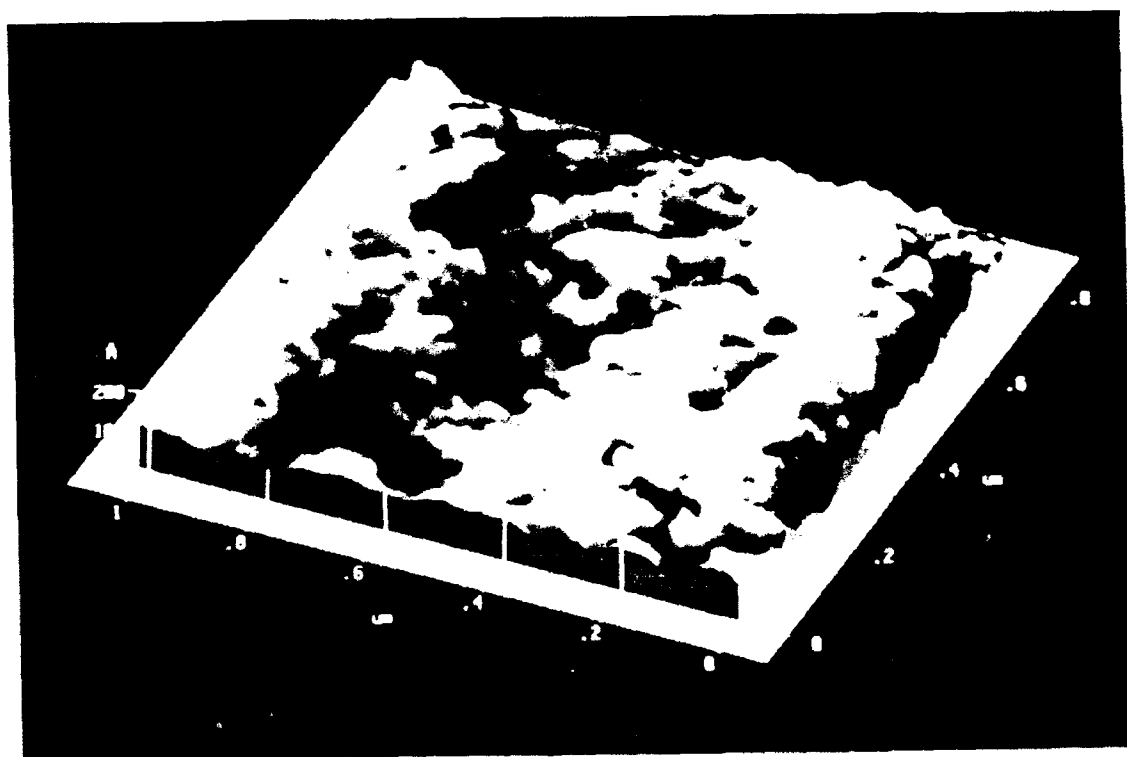


Figure 2. Topographic (constant current) STM micrograph of the surface morphology of the as-deposited SiGe film following a high-temperature anneal at 850 °C in a vacuum of 10^{-8} Torr for 30 min.

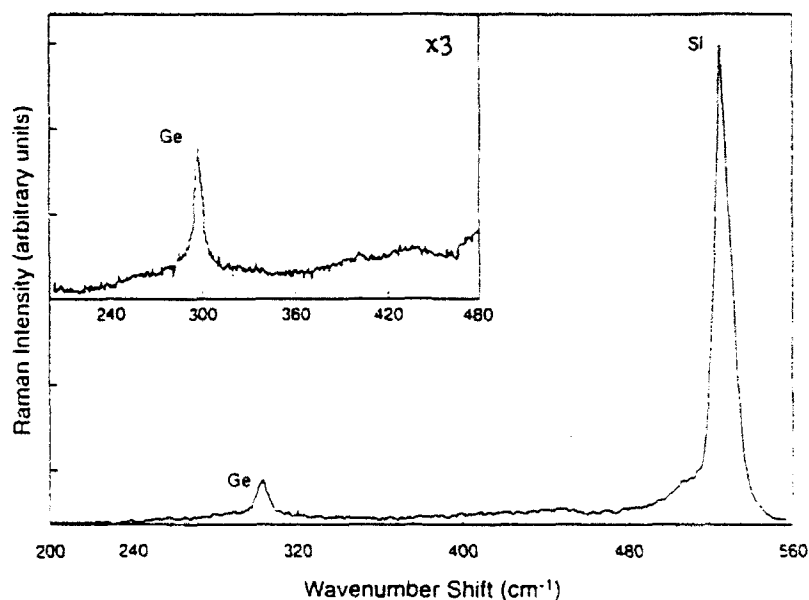


Figure 3. Raman spectrum of the SiGe film deposited on natural C(001) diamond substrates.

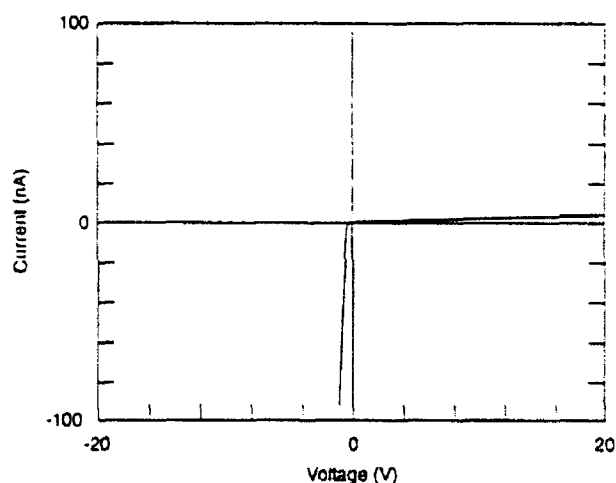


Figure 4. Linear plot of the current-voltage (I-V) characteristics of the SiGe contacts on semiconducting diamond C(001) substrates. Measurements were conducted at 25 °C.

Shown in Fig. 5 is the corresponding I-V characteristics for the high-temperature annealed SiGe contacts recorded at 25 °C.

Clearly, in comparison with the as-deposited films, the rectifying behavior of the annealed SiGe contacts has been degraded. In particular, the forward bias turn-on voltage has been significantly reduced. From the I-V measurements a forward bias turn-on voltage of ~ 0.2 V

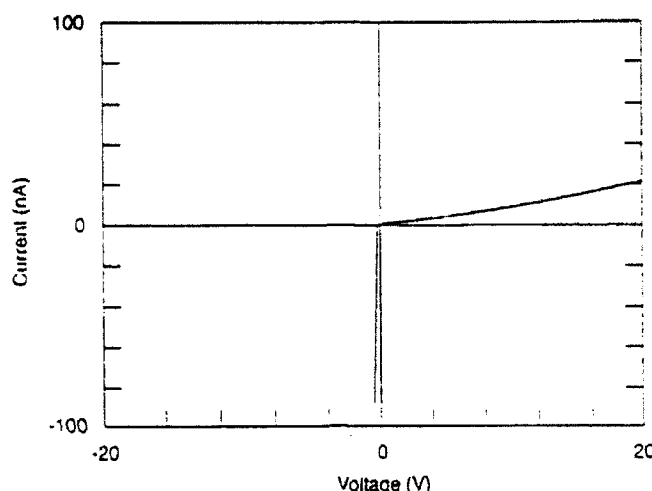


Figure 5. I-V characteristics of the post-growth high-temperature annealed SiGe contacts at 25 °C.

has been estimated. Also, the reverse bias leakage current has increased to ~22 nA which corresponds to a current density of $7.3 \times 10^{-6} \text{ A/cm}^2$ at 20 V. In addition, corresponding I-V measurements conducted at 300 °C showed ohmic-like behavior.

D. Conclusions

In summary SiGe films have been grown by the co-deposition of Si and Ge on natural single crystal diamond C(001) substrates. As evidenced by LEED and STM analysis, the as-deposited films are polycrystalline. The I-V measurements of the SiGe contacts have demonstrated rectifying characteristics at room temperature. However, for measurements conducted at 300 °C the I-V characteristics exhibit ohmic-like behavior. Furthermore, it has also been demonstrated that subsequent post-growth annealing of the contacts has degraded the I-V characteristics.

E. Future Research Plans

Optimize the substrate cleaning procedure and growth conditions to achieve epitaxial SiGe films. Measurement of the bandgap offset between the SiGe contacts and the single crystal diamond substrate utilizing ultraviolet photoelectron spectroscopy (UPS).

F. Acknowledgements

TPH and RJN gratefully acknowledge partial support from the Office of Naval Research (Contract No. N00014-92-J-1477) and Kobe Research Laboratories, USA.

G. References

1. M. W. Geis, N. N. Efremow and D. D. Rathman, *J. Vac. Sci. Technol.* **6**, 1953 (1988).
2. For a review see K. Das, V. Venkatesan, K. Miyata, D. L. Dreifus and J. T. Glass, *Thin Solid Films* **212**, 19 (1992).
3. K. L. Moazed, J. R. Zeidler and M. J. Taylor, *J. Appl. Phys.* **68**, 2246 (1990).
4. T. P. Humphreys, J. V. LaBrasca, R. J. Nemanich, K. Das and J. B. Posthill, *Jpn. J. Appl. Phys.* **30**, L1409 (1991).
5. T. P. Humphreys, J. V. LaBrasca, R. J. Nemanich, K. Das and J. B. Posthill, *Electron. Lett.* **27**, 1515 (1991).
6. V. Venkatesan, D. G. Thompson and K. Das, *Proceedings of Symp. Mater. Res. Soc.* **270**, 419 (1992).
7. P. C. Kelires and J. Tersoff, *Phys. Rev. B* **63**, 1164 (1989).

V. Distribution List

Mr. Max Yoder Office of Naval Research Electronics Program--Code 1114 800 North Quincy Street Arlington, VA 22217	3
Office of Naval Research Resident Representative The Ohio State Univ. Research Center 1960 Kenny Road Columbus, OH 43210-1063	2
Director Naval Research Laboratory Attention: Code 2627 Washington, DC 20314	1
Defense Technical Information Center Building 5 Cameron Station Alexandria, VA 22314	4