

1-1-1999

Nitrogen incorporation and trace element analysis of nanocrystalline diamond thin films by secondary ion mass spectrometry

D. Zhou

University of Central Florida

F. A. Stevie

L. Chow

University of Central Florida

J. McKinley

H. Gnaser

Find similar works at: <https://stars.library.ucf.edu/facultybib1990>

See next page for additional authors
University of Central Florida Libraries <http://library.ucf.edu>

This Article; Proceedings Paper is brought to you for free and open access by the Faculty Bibliography at STARS. It has been accepted for inclusion in Faculty Bibliography 1990s by an authorized administrator of STARS. For more information, please contact STARS@ucf.edu.

Recommended Citation

Zhou, D.; Stevie, F. A.; Chow, L.; McKinley, J.; Gnaser, H.; and Desai, V. H., "Nitrogen incorporation and trace element analysis of nanocrystalline diamond thin films by secondary ion mass spectrometry" (1999).

Faculty Bibliography 1990s. 2916.

<https://stars.library.ucf.edu/facultybib1990/2916>

Authors

D. Zhou, F. A. Stevie, L. Chow, J. McKinley, H. Gnaser, and V. H. Desai

Nitrogen incorporation and trace element analysis of nanocrystalline diamond thin films by secondary ion mass spectrometry

D. Zhou, F. A. Stevie, L. Chow, J. McKinley, H. Gnaser, and V. H. Desai

Citation: *Journal of Vacuum Science & Technology A* **17**, 1135 (1999); doi: 10.1116/1.581786

View online: <https://doi.org/10.1116/1.581786>

View Table of Contents: <https://avs.scitation.org/toc/jva/17/4>

Published by the [American Vacuum Society](#)


ARTICLES YOU MAY BE INTERESTED IN

[Bonding structure in nitrogen doped ultrananocrystalline diamond](#)

Journal of Applied Physics **93**, 5606 (2003); <https://doi.org/10.1063/1.1564880>

[Synthesis and electron field emission of nanocrystalline diamond thin films grown from \$N_2/CH_4\$ microwave plasmas](#)


Journal of Applied Physics **82**, 4546 (1997); <https://doi.org/10.1063/1.366190>



Instruments for Advanced Science


Contact Hiden Analytical for further details:
W www.HidenAnalytical.com
E info@hiden.co.uk

[CLICK TO VIEW](#) our product catalogue



Gas Analysis

- dynamic measurement of reaction gas streams
- catalysis and thermal analysis
- molecular beam studies
- dissolved species probes
- fermentation, environmental and ecological studies




Surface Science

- UHV TPD
- SIMS
- end point detection in ion beam etch
- elemental imaging - surface mapping



Plasma Diagnostics

- plasma source characterization
- etch and deposition process reaction kinetic studies
- analysis of neutral and radical species



Vacuum Analysis

- partial pressure measurement and control of process gases
- reactive sputter process control
- vacuum diagnostics
- vacuum coating process monitoring

Nitrogen incorporation and trace element analysis of nanocrystalline diamond thin films by secondary ion mass spectrometry

D. Zhou^{a),b)}

Advanced Materials Processing and Analysis Center, University of Central Florida, Orlando, Florida 32816

F. A. Stevie

Cirent Semiconductor, Orlando, Florida 32819

L. Chow^{c)}

Advanced Materials Processing and Analysis Center, University of Central Florida, Orlando, Florida 32816

J. McKinley

Cirent Semiconductor, Orlando, Florida 32819

H. Gnaser

Department of Physics, University of Kaiserslautern, D-67663 Kaiserslautern, Germany

V. H. Desai^{a)}

Advanced Materials Processing and Analysis Center, University of Central Florida, Orlando, Florida 32816

(Received 2 November 1998; accepted 3 May 1999)

Nitrogen has been successfully incorporated into nanocrystalline diamond films produced by a CH₄/N₂ microwave plasma-enhanced chemical vapor deposition method. High mass resolution secondary ion mass spectrometry (SIMS) characterization shows that the density of the incorporated nitrogen, monitored via CN⁻, can be as high as 10²¹ atoms/cm³, depending on the ratio of CH₄ to N₂ in the reactant gas and on the substrate temperature used for the film preparation. SIMS depth profiles demonstrate that the incorporated nitrogen is uniform within the diamond films (about 1.5 μm thick) except at the surfaces and at the interface between film and substrate. Furthermore, the SIMS analyses reveal that alkali elements such as Na, K, and Li appear to be contaminants at the surface of nanocrystalline diamond films produced using a CH₄/Ar or CH₄/H₂ discharge, but are bulk impurities only for the films prepared using a CH₄/N₂ plasma. These alkali impurities can play an important role in electronic properties such as electron field emissions of nanocrystalline diamond thin films. © 1999 American Vacuum Society. [S0734-2101(99)22604-8]

I. INTRODUCTION

Nanocrystalline diamond films have been successfully produced from plasma-enhanced chemical vapor deposition (PECVD) using a mixture of CH₄/N₂ or CH₄/Ar as the reactant gas.¹⁻³ In addition to high thermal conductivity, low dielectric constant, and excellent radiation hardness, nanocrystalline diamonds have both the grain size and the surface roughness in the nanometer scale that contribute significantly to applications of nanocrystalline diamond films as protective coatings for optical devices or as electron field emitters for flat panel displays.⁴⁻⁶ However, the optical and electrical properties of nanocrystalline diamond films depend strongly on impurities such as nitrogen and sodium, which may be introduced into the films during the deposition processes.⁷ In order to better understand the properties of nanocrystalline diamond films and to realize its unique applications as an optical or electronic material, it is important to systemically

study the impurities or trace elements in nanocrystalline diamond films produced using chemical vapor deposition (CVD) with different reactant gases.

Nitrogen has been recognized as an important impurity in diamond, and the nature of its electronic states has been a concern in elucidating the semiconductor properties of both natural and synthetically grown diamonds.⁸ Although the substitutional nitrogen in a diamond film is a deep donor impurity with a level at 1.9 eV below the minimum of the conduction band,⁹ nitrogen impurities can affect the optical transparency,¹⁰ the thermal conductivity,¹¹ and electron field emission^{12,2} of diamond films. Moreover, the effects of nitrogen as an addition or impurity in the reactant gas on the properties of the resulting CVD diamond films have been extensively studied,¹³⁻¹⁵ and the incorporation of nitrogen impurities has been investigated by directly adding nitrogen to the reactant gas during the film deposition process.^{16,17} Unfortunately, the uniform incorporation of nitrogen into CVD diamonds has been extremely difficult, presumably because the reactant gas used for film growth is rich in hydrogen, which has a strong etching effect on any non-diamond phase deposition. Furthermore, no successful method has been found to control the concentration of incorporated nitrogen in CVD diamond films.

In contrast to the study of nitrogen as a substitutional

^{a)}Also at: Department of Mechanical, Materials, and Aerospace Engineering, University of Central Florida, Orlando, FL 32816.

^{b)}Electronic mail: dzhou@pegasus.cc.ucf.edu

^{c)}Also at: Department of Physics, University of Central Florida, Orlando, FL 32816.

impurity, lithium and sodium are promising interstitial impurities for diamonds. The energies of Li and Na impurities in interstitial and substitutional positions have been calculated, and the interstitial sites were found to be energetically favored.¹⁸ The activation energies of 0.1 and 0.3 eV below the conduction band minimum have been computed for Li and Na, respectively. Consequently, the electronic properties of diamonds may be strongly affected by the presence of these impurities even though the solubility of Li and Na in diamond is very low.^{19–21} However, the theoretical results have not been confirmed by experimental data because a high density of structural defects is associated with the introduction of Na or Li into diamonds by forced diffusion or ion implantation methods. A high density of Li or Na in diamond would be required for a useful electronic effect because the activation is no more than one percent. Therefore, it is important to investigate Li, Na, and K impurities in nanocrystalline diamond films in order to reveal how these impurities affect the applications of nanocrystalline diamonds as optical or electronic materials. Further, developing a simple method of properly introducing the alkaline elements as impurities into nanocrystalline diamond will be of great scientific and technological significance.

In this article, we report that nitrogen is a major impurity of nanocrystalline diamond films prepared using a CH₄/N₂ microwave discharge. High mass resolution secondary ion mass spectrometry (SIMS) analysis shows that the density of incorporated nitrogen in nanocrystalline diamond films depends considerably on the deposition conditions, such as the composition of the reactant gas and the substrate temperature. In addition, elements such as Na, K, and Li in the CVD nanocrystalline diamond films prepared from CH₄/N₂, or CH₄/Ar, or CH₄/H₂ microwave discharge have been characterized. Based on SIMS analyses, the effects of discharge chemistry on the incorporation of nitrogen and alkali metals into nanocrystalline diamond films during the deposition processes have been considered.

II. EXPERIMENT

Nanocrystalline diamond films were made using an ASTeX microwave PECVD system. Mixtures of CH₄ and N₂ with different ratios were used as the reactant gases for nanocrystalline diamond deposition. *N*-type single-crystal silicon wafers with ⟨100⟩ orientation were used as the substrates, and mechanical polishing with fine diamond powder (0.1 μm in size) was employed to provide nucleation sites for nanocrystalline diamond film growth. During the deposition processes, the substrate temperature, input microwave power, and total ambient pressure were normally kept at 800 °C, 1100 W, and 35 Torr, respectively. In order to investigate the effect of the processing parameters on the properties of the resulting films, nanocrystalline diamond films have also been prepared at different substrate temperatures and with different ratios of CH₄ to N₂, respectively. Moreover, mixtures of CH₄/Ar or CH₄/H₂ were employed as the reactant gas to explore the effect of the discharge chemistry on the impurities in the nanocrystalline diamonds. Note that research

grade (99.999%) reactant gases were used in this study. The films used for SIMS analyses were approximately 1.5 μm thick, and the thickness of the films was determined by using an *in situ* laser reflectance interferometer to monitor the modulations of the surface reflectivity during the film growth. The as-grown films from different microwave discharges were analyzed using a CAMECA IMS-3f SIMS instrument with either O₂⁺ beam at 5.5 keV impact energy or Cs⁺ beam at 14.5 keV impact energy. Note that O₂⁺ beam was used for the depth profiling of Na, K, and Li in the nanocrystalline diamond films, while Cs⁺ was used for monitoring the distribution of nitrogen. During SIMS depth profiling, the typical current and raster size of the primary beam were 100 nA and 250 μm, respectively, with a detected area of 60 μm diameter. SIMS analyses of diamond films with good depth resolution have been shown to be possible without charge neutralization.^{22–26}

III. RESULTS AND DISCUSSIONS

SIMS analysis at low-mass resolution cannot successfully characterize the incorporated nitrogen in diamond thin films because of the interference of hydrocarbon masses with positive nitrogen secondary ions, which have low ion yield, and because of a lack of stable negative nitrogen ions. In contrast, CN⁻ does have good secondary ion yield. Therefore, high-mass resolution SIMS was employed to separate CN⁻ negative secondary ions with a mass of 26.003 amu from C₂H₂⁻ with a mass of 26.015 amu which requires a mass resolution ($m/\Delta m$) of about 1700 to separate these two masses. However, a mass resolution of approximately 7030 is needed to separate CN⁻ from ¹³C₂⁻, which was not resolved from CN⁻ in this study. Because ¹³C is only 1% of carbon which has a density of 1.8×10^{23} atoms/cm³ in diamond, the fraction of ¹³C₂⁻ compared with ¹²C₂⁻ is 1×10^{-4} , meaning that the possible concentration of ¹³C₂⁻ would be $\sim 1 \times 10^{19}$ atoms/cm³. Figure 1(a) displays the SIMS depth profiles of carbon, nitrogen (CN⁻), and silicon (²⁸Si⁻), illustrating that the density of the incorporated nitrogen is as high as $\sim 8 \times 10^{20}$ atoms/cm³ with a uniform distribution within the 1.5 μm thick nanocrystalline diamond film made from a microwave plasma with mixture of 4 vol % CH₄ and 96 vol % N₂ in the reactant gas. The density scale is established using relative sensitivity factors derived from implantation standards, and 1.8×10^{23} atoms/cm³ is used as the (average) carbon density of diamond for the calibration. Besides nitrogen, the SIMS depth profile also shows that nanocrystalline diamond films prepared using a CH₄/N₂ microwave plasma also contain a significant amount of hydrogen, which may be trapped at the grain boundaries of nanocrystalline diamond films to terminate carbon-dangling bonds. Note that hydrogen trapped at the grain boundaries comes from hydrocarbon (CH₄) used in the reactant gas. Oxygen (¹⁶O⁻) has also been observed as an impurity in the film, which may be due to the Si substrate containing some SiO₂ at the surface even after the mechanical polishing with diamond powder. Figure 1(b) shows SIMS depth profiles of nitrogen (²⁶CN⁻), hydrogen (¹H⁻), oxygen (¹⁶O⁻), silicon

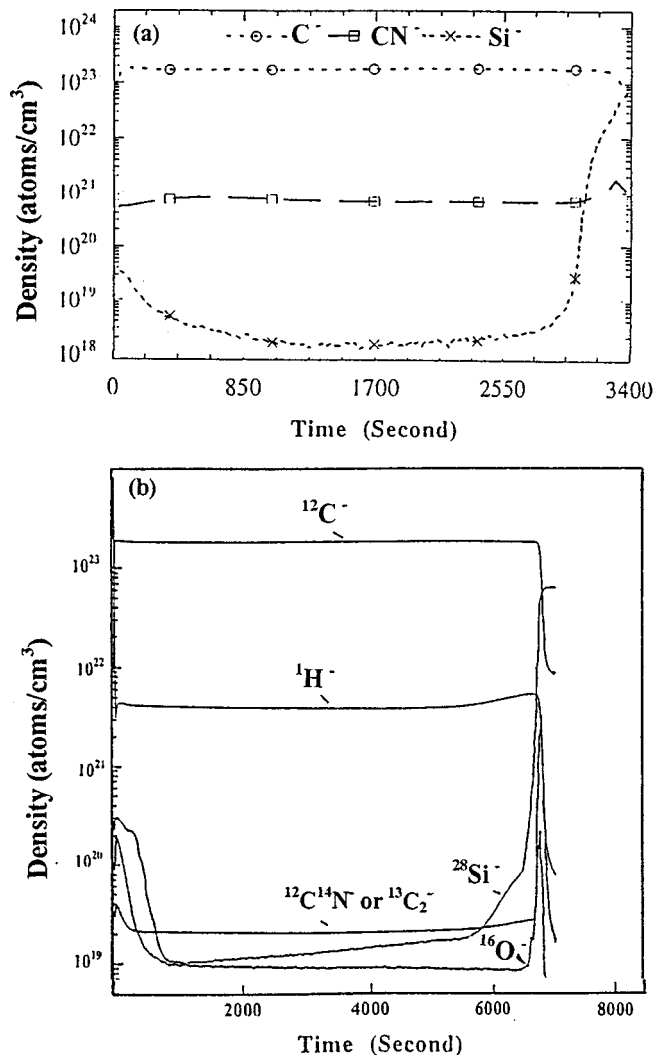


FIG. 1. (a) SIMS depth profile of nitrogen ($^{26}\text{CN}^-$), oxygen ($^{16}\text{O}^-$), silicon ($^{28}\text{Si}^-$), and carbon ($^{12}\text{C}^-$) in the nanocrystalline diamond film prepared from a CH_4/N_2 discharge; and (b) depth profile of nitrogen ($^{26}\text{CN}^-$), oxygen ($^{16}\text{O}^-$), silicon ($^{28}\text{Si}^-$), and carbon ($^{12}\text{C}^-$) in nanocrystalline diamond produced from a CH_4/Ar discharge.

($^{28}\text{Si}^-$), and carbon ($^{12}\text{C}^-$) in the nanocrystalline diamond film prepared using a CH_4/Ar discharge, demonstrating a relatively low density of nitrogen impurity (1.2×10^{19} atoms/cm 3) being incorporated in the nanocrystalline diamond film during the deposition processing. Notice that the $^{13}\text{C}_2^-$ background could also account for this apparent low level of nitrogen. This observation suggests that the nitrogen plasma used for the nanocrystalline diamond deposition significantly enhance the incorporation of nitrogen.

Figure 2 shows a plot of density of the incorporated nitrogen, obtained from SIMS depth profiles, in the nanocrystalline diamond thin films prepared using CH_4/N_2 microwave discharges with different concentrations of N_2 in the reactant gases. Note that the other processing parameters such as input microwave power (1100 W) and substrate temperature (800 °C) were kept the same when the concentration of N_2 in the reactant gas was changed for each deposition. The plot demonstrates that the density of incorporated

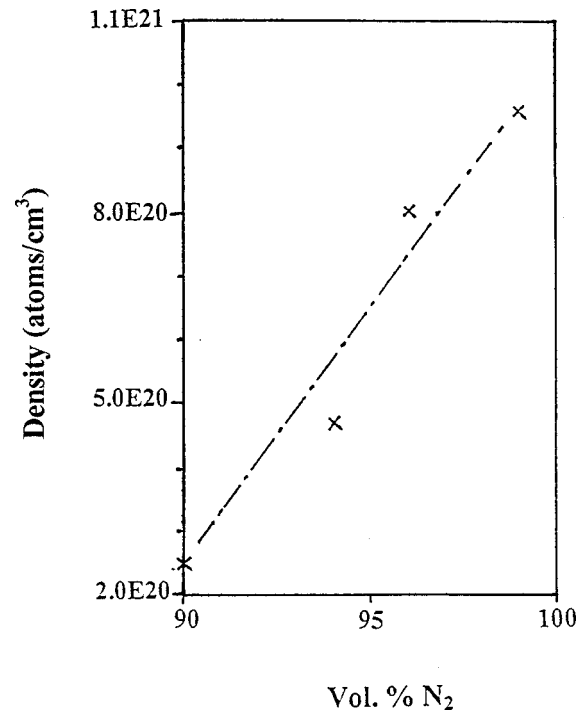


FIG. 2. Plot of density of incorporated nitrogen in the nanocrystalline diamond thin films versus concentration of N_2 in the reactant gases used for CVD process.

nitrogen in the nanocrystalline diamond films increases linearly when the volume percentage of N_2 in the reactant gas is increased from 90% to 99% and the content of CH_4 is decreased accordingly. For instance, the density of nitrogen impurity in the film, produced from a reactant gas with 1 vol % CH_4 and 99 vol % N_2 , is approximately 9.5×10^{20} atoms/cm 3 . In contrast, if the reactant gas with 10 vol % CH_4 and 90 vol % N_2 is used for the processing at 800 °C, the density of nitrogen impurity is reduced to 2.4×10^{20} atoms/cm 3 . This result, therefore, indicates that increasing the concentration of nitrogen in the gas phase directly increases the possibility of incorporating nitrogen into the resulting films, while decreasing the content of CH_4 in the gas phase results in generating less atomic hydrogen in the discharge. Atomic hydrogen has a strong etching effect on a nondiamond phase such as nitrogen at the nanocrystalline diamond growth surface. The SIMS depth profiles of these samples also reveal uniform distributions of the incorporated nitrogen for all the nanocrystalline diamond films analyzed here.

The effect of substrate temperature used for nanocrystalline diamond deposition on the incorporation of nitrogen has also been investigated using SIMS depth profiling. Figure 3 shows a plot of density of incorporated nitrogen in the nanocrystalline diamonds prepared using a microwave discharge with a mixture of 4 vol % CH_4 and 96 vol % N_2 as the reactant gas versus the substrate temperature, which indicates that the density changes from 1.15×10^{21} to 1.2×10^{20} atoms/cm 3 when the substrate temperature used for nanocrystalline diamond deposition is increased from 400 to

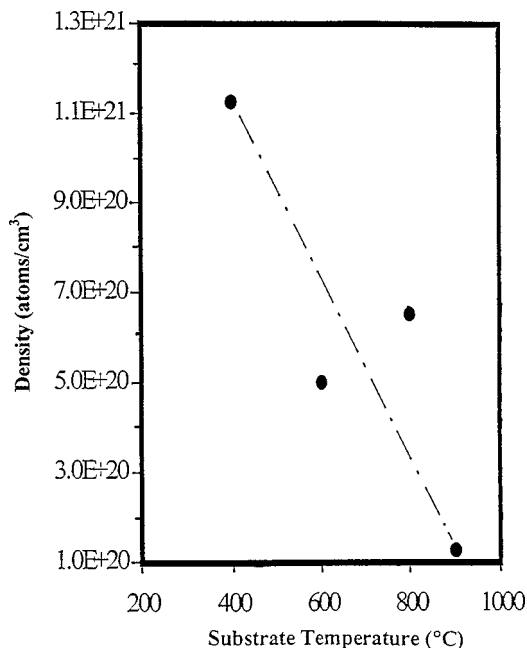


Fig. 3. Plot of density of incorporated nitrogen in the nanocrystalline diamonds versus substrate temperature used for CVD process in which a mixture of CH_4/N_2 was employed as the reactant gas.

900 °C. More nitrogen remains in nanocrystalline diamond coatings when a lower substrate temperature is used for the deposition.

In order to quantitatively characterize Na, K, and Li impurities in nanocrystalline diamonds made using microwave discharges, a standard sample was carefully prepared by using ion implantation of Na, K, and Li, each with a dose of 5×10^{13} atoms/cm² at room temperature. The energies used for the implantation of Li, Na, and K were 20, 50, and 80 keV, respectively. Figure 4 shows a depth profile of ⁷Li, ²³Na, and ³⁹K from the standard ion-implanted sample, prepared by Charles Evans & Assoc., in which these three ele-

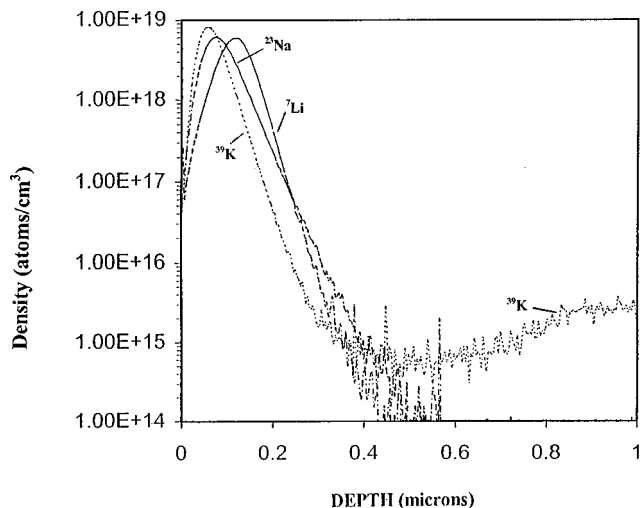


Fig. 4. SIMS depth profiles of ⁷Li, ²³Na, and ³⁹K in a standard sample in which these three elements were implanted into the nanocrystalline diamond together.

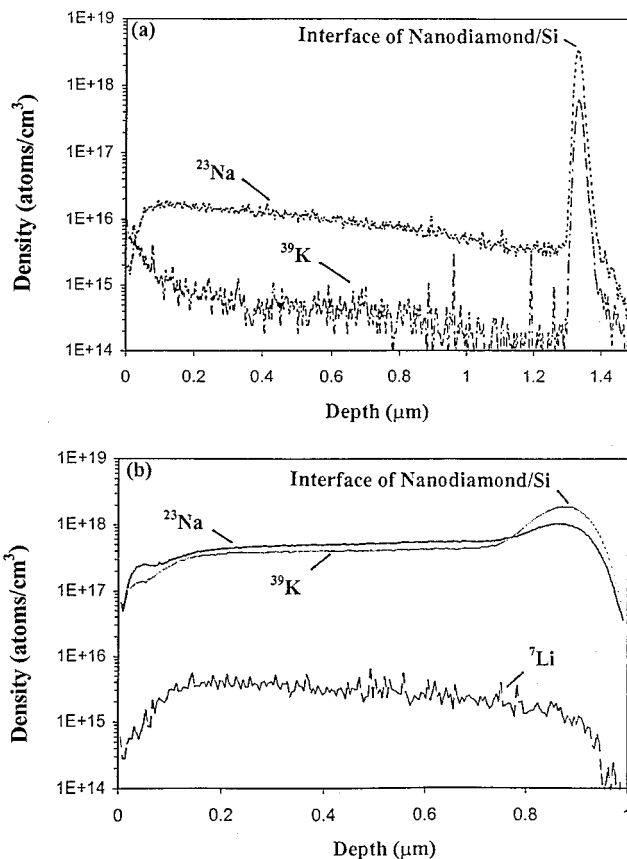


Fig. 5. SIMS depth profiles of the nanocrystalline diamond coatings produced from (a) CH_4/Ar and (b) CH_4/N_2 microwave discharges.

ments were implanted into a nanocrystalline diamond film. Note that the SIMS depth profile of the standard sample shows an almost ideal Gaussian distribution for each implanted element, and demonstrates excellent detection limits for these three elements using SIMS. Note also that this diamond film, prepared using a microwave discharge with a mixture of 4 vol % CH_4 and 96 vol % H_2 as the reactant gas, has low densities of Li, Na, and K as contaminants, which are at background level.

The other as-grown nanocrystalline diamond films prepared using different microwave discharges were then characterized quantitatively using SIMS depth profiling in order to measure the distributions of Na, K, and Li introduced during the deposition process. Figure 5 shows SIMS depth profiles of the nanocrystalline diamond coatings produced using (a) CH_4/Ar and (b) CH_4/N_2 discharges, respectively. The depth profiles shown in Fig. 5(a) demonstrate that only the surfaces or interfaces of nanocrystalline diamond films prepared using CH_4/Ar discharge are contaminated by Na and K, but in the bulk of the films the densities of these elements are at the background level, and no Li has been detected in this sample. In contrast, for the nanocrystalline diamond films prepared using a CH_4/N_2 discharge, the SIMS depth profiles shown in Fig. 5(b) illustrate that Na, K, and Li are not only at the surface, but also through the bulk of the films. The densities of these impurities are also increased significantly when a CH_4/N_2 discharge is employed. Further-

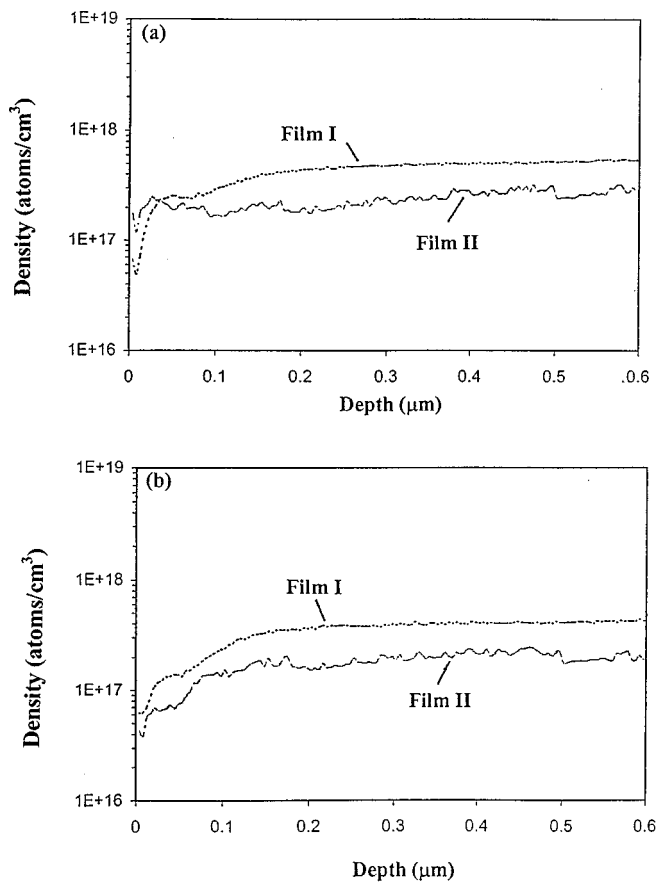


FIG. 6. SIMS depth profiles of (a) ^{23}Na and (b) ^{39}K in nanocrystalline diamonds produced from nitrogen discharge with different ratios of CH_4 and N_2 in the reactant gas (Film I: 4% CH_4 +96% N_2 and film II: 15% CH_4 +85% N_2).

more, Fig. 6 shows the depth profiles of Na [see Fig. 6(a)] and K [see Fig. 6(b)] in nanocrystalline diamond films produced using nitrogen discharge with different ratios of CH_4 and N_2 in the reactant gas at substrate temperature of 800 °C. Film I was deposited from the reactant gas with 4 vol % CH_4 and 96 vol % N_2 , while film II was from the gas with 15 vol % CH_4 and 85 vol % N_2 . Other processing parameters were kept at constant values during the film depositions. As shown in the profiles, the densities of Na and K impurities in the films decrease by a factor 2 when the ratio of CH_4 and N_2 in the reactant gas increases from 0.04 to 0.17. This result again indicates that discharge chemistry may play an important role in the incorporation of alkali impurities in nanocrystalline diamond films. The reason that a CH_4/N_2 microwave discharge introduces significant Na and K contamination is not fully understood yet. The contamination may come from the nitrogen gas used for the CVD process, even though the gas is of high research grade (99.999%), or from the deposition system. The high densities of contaminants at the nanocrystalline diamond/silicon interface are probably the result of processing, for example, mechanical polishing of the silicon substrate before diamond deposition.

Introducing the alkaline elements as impurities into CVD diamond film by forced diffusion and implantation methods

has been extensively studied.^{27,28} Conventional ion implantation introduces structural (vacancy and interstitial) defects that are difficult to remove because it is very difficult to anneal diamond. Moreover, the atomic radii of Na and K are too large for diffusion through the diamond lattice, in which the lattice distortions will be very strong. Therefore, the forced incorporations of Na and K in CVD diamond have not been successful to date. It has also been reported that Na can be embedded into the growing diamond layer during the deposition process.²⁹ When nanocrystalline diamond films are deposited using a CH_4/N_2 microwave discharge, nitrogen plasma enhances significantly the incorporations of nitrogen, sodium, and potassium in the nanocrystalline diamonds. This suggests that the alkaline elements as the impurities can be incorporated in nanocrystalline diamond films during the deposition process with the assistance of nitrogen plasma. Note that intention of this work is to properly introduce the alkali impurities into the deposition system and to control the densities of these impurities in the nanocrystalline diamonds. The incorporation of nitrogen in nanocrystalline diamond films can be controlled by using a mixture of three gases such as CH_4 , Ar, and N_2 . In this gas system, a change of the nitrogen concentration can be balanced by Ar gas, and the amount of CH_4 in the discharge can be kept as the constant that is important for obtaining a high quality nanocrystalline diamond coating.

IV. CONCLUSIONS

High mass resolution SIMS analyses using a Cs^+ beam demonstrate that the density of the incorporated nitrogen in nanocrystalline diamond coatings deposited from a nitrogen discharge, monitored via CN^- , can be as high as 10^{21} atoms/ cm^3 with a uniform distribution through the films. In contrast, nitrogen in the nanocrystalline diamond films prepared using a CH_4/Ar plasma is at or below 1.2×10^{19} atoms/ cm^3 , which also can be the background due to $^{13}\text{C}_2^-$. Detailed SIMS analyses also reveal that the incorporation of nitrogen impurity in nanocrystalline diamonds films depends on the ratio of CH_4 to N_2 in the reactant gas and on the substrate temperature used for the film preparation. When the ratio of CH_4 to N_2 in the reactant gas changes from 1:99 to 10:90, the density of the incorporated nitrogen in the resulting film decreases from 9.5×10^{20} to 2.4×10^{20} atoms/ cm^3 . As the substrate temperature decreases from 900 to 400 °C, the incorporated nitrogen in nanodiamond coatings is increased from 1.2×10^{20} to 1.15×10^{21} atoms/ cm^3 .

SIMS analyses also demonstrate that the alkali impurities (Na, K, and Li) in nanocrystalline diamond films are considerably enhanced using a nitrogen discharge to prepare the diamond coatings. The densities of Na and K in these nanocrystalline diamond films are in the range of several ppms, and are affected greatly by the CVD processing conditions, particularly the discharge chemistry. For the nanocrystalline diamond films produced from argon or hydrogen discharges, the densities of Na, K, and Li are very low compared with

the nanocrystalline diamond films produced from nitrogen plasma.

ACKNOWLEDGMENTS

The authors would like to acknowledge the financial and technical support from the Advanced Materials Processing and Analysis Center and UCF/Cirent Materials Characterization Facility at University of Central Florida. D. Z. specially thanks D. M. Gruen and A. R. Krauss from Argonne National Laboratories for valuable discussions.

- ¹D. Zhou, A. R. Krauss, L. C. Qin, T. G. McCauley, D. M. Gruen, T. D. Corrigan, R. P. H. Chang, and H. Gnaser, *J. Appl. Phys.* **82**, 4546 (1997).
- ²D. Zhou, T. G. McCauley, L. C. Qin, A. R. Krauss, and D. M. Gruen, *J. Appl. Phys.* **83**, 540 (1998).
- ³D. Zhou, D. M. Gruen, L. C. Qin, T. G. McCauley, and A. R. Krauss, *J. Appl. Phys.* **84**, 1981 (1998).
- ⁴C. Moelle, M. Werner, F. Szucs, D. Wittorf, M. Sellschoop, J. von Borany, H. J. Fecht, and C. Johnston, *Diamond Relat. Mater.* **7**, 499 (1998).
- ⁵D. M. Bhusari, J. R. Yang, T. Y. Wang, K. H. Chen, S. T. Lin, and L. C. Chen, *J. Mater. Res.* **13**, 1769 (1998).
- ⁶D. Zhou, A. R. Krauss, T. D. Corrigan, T. G. McCauley, R. P. H. Chang, and D. M. Gruen, *J. Electrochem. Soc.* **144**, L224 (1997).
- ⁷G. Popovici and M. A. Prelas, *Diamond Relat. Mater.* **4**, 1305 (1995).
- ⁸S. A. Kajihara, A. Antonelli, J. Bernholc, and R. Car, *Phys. Rev. Lett.* **66**, 2010 (1991).
- ⁹R. G. Farrer, *Solid State Commun.* **7**, 685 (1969).
- ¹⁰W. Kaiser and W. L. Bond, *Phys. Rev.* **115**, 857 (1959).
- ¹¹R. Berman, P. R. W. Hudson, and M. Martinez, *J. Phys.* **18**, 1430 (1975).
- ¹²M. W. Geis, J. C. Twichell, J. Macaulay, and K. Okano, *Appl. Phys. Lett.* **67**, 1328 (1995).
- ¹³A. Badzian, T. Badzian, and S. T. Lee, *Appl. Phys. Lett.* **62**, 3432 (1993).
- ¹⁴R. Locher, C. Wild, N. Herres, D. Behr, and P. Koidl, *Appl. Phys. Lett.* **65**, 34 (1994).
- ¹⁵S. Jin and T. D. Moustakes, *Appl. Phys. Lett.* **65**, 403 (1994).
- ¹⁶J. Mort, M. A. Machonkin, and K. Okumura, *Appl. Phys. Lett.* **59**, 3148 (1991).
- ¹⁷H. Spicka, M. Griesser, H. Hutter, M. Grasserbauer, S. Bohr, R. Haubner, and B. Lux, *Diamond Relat. Mater.* **5**, 383 (1996).
- ¹⁸J. Bernholc, S. A. Kajihara, and A. Antonelli, in *MRS Proceedings On New Diamond Science and Technology*, edited by R. Messier, J. T. Glass, J. E. Butler, and R. Roy (Materials Research Society, Pittsburgh, 1991), p. 923.
- ¹⁹J. F. Prins, *Diamond Relat. Mater.* **4**, 580 (1995).
- ²⁰S. Prawer, C. U. Saguy, G. Braunstein, and R. Kalish, *Appl. Phys. Lett.* **63**, 2502 (1993).
- ²¹K. Okumura, J. Mort, and M. Machonkin, *Appl. Phys. Lett.* **57**, 1907 (1990).
- ²²S. P. Smith and R. G. Wilson, Second International Symposium on Diamond Films, Minks Belarus, 3–5 May 1994.
- ²³R. G. Wilson, *Surf. Coat. Technol.* **47**, 559 (1991).
- ²⁴S. P. Smith, M. I. Landstrass, and R. G. Wilson, in *Secondary Ion Mass Spectrometry SIMS VII*, edited by A. Benninghoven, K. T. F. Janssen, J. Tumper, and H. W. Werner (Wiley, New York, 1992), p. 159.
- ²⁵R. G. Wilson, C. L. Kirshbaum, G. E. Lux, S. P. Smith, and C. Hitzman, in *Secondary Ion Mass Spectrometry SIMS VII*, edited by A. Benninghoven, K. T. F. Janssen, J. Tumper, and H. W. Werner (Wiley, New York, 1992), p. 151.
- ²⁶R. G. Wilson, *J. Mass Spectrom.* **143**, 43 (1995).
- ²⁷J. F. Prins, *Mater. Sci. Rep.* **7**, 271 (1992).
- ²⁸G. Popovici, T. Sung, M. A. Prelas, S. Khasawinah, and R. G. Wilson, *J. Appl. Phys.* **77**, 5625 (1995).
- ²⁹K. D. Jamison, H. K. Schmidt, D. Eisenmann, and R. P. Hellmer, *Mater. Res. Soc. Symp. Proc.* **302**, 251 (1993).