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

D. Zhou\textsuperscript{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\textsuperscript{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\textsuperscript{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 CH\textsubscript{4}/N\textsubscript{2} 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\textsuperscript{–}, can be as high as 10\textsuperscript{21} atoms/cm\textsuperscript{3}, depending on the ratio of CH\textsubscript{4} to N\textsubscript{2} 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 \textmu m 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 CH\textsubscript{4}/Ar or CH\textsubscript{4}/H\textsubscript{2} discharge, but are bulk impurities only for the films prepared using a CH\textsubscript{4}/N\textsubscript{2} 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 CH\textsubscript{4}/N\textsubscript{2} or CH\textsubscript{4}/Ar as the reactant gas.\textsuperscript{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.\textsuperscript{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.\textsuperscript{3} 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 systematically 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.\textsuperscript{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,\textsuperscript{9} nitrogen impurities can affect the optical transparency,\textsuperscript{10} the thermal conductivity,\textsuperscript{11} and electron field emission\textsuperscript{12,13} 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.\textsuperscript{13–15} The incorporation of nitrogen impurities has been investigated by directly adding nitrogen to the reactant gas during the film deposition process.\textsuperscript{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...
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. 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. 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 alkali 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 CH$_4$/N$_2$ 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 CH$_4$/N$_2$, or CH$_4$/Ar, or CH$_4$/H$_2$ 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 CH$_4$ and N$_2$ 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 CH$_4$ to N$_2$, respectively. Moreover, mixtures of CH$_4$/Ar or CH$_4$/H$_2$ 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 O$_2^+$ beam at 5.5 keV impact energy or Cs$^+$ beam at 14.5 keV impact energy. Note that O$_2^+$ 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.

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 C$_2$H$_2^+$ with a mass of 26.015 amu which requires a mass resolution ($m/Δm$) of about 1700 to separate these two masses. However, a mass resolution of approximately 7030 is needed to separate CN$^-$ from $^{13}$C$_2^-$, which was not resolved from CN$^-$ in this study. Because $^{13}$C is only 1% of carbon which has a density of $1.8×10^{23}$ atoms/cm$^3$ in diamond, the fraction of $^{13}$C$_2^-$ compared with $^{12}$C$_2^-$ is $1×10^{-4}$, meaning that the possible concentration of $^{13}$C$_2^-$ would be $1×10^{19}$ atoms/cm$^2$. Figure 1(a) displays the SIMS depth profiles of carbon, nitrogen (CN$^-$), and silicon ($^{28}$Si$^-$), illustrating that the density of the incorporated nitrogen is as high as $8×10^{20}$ atoms/cm$^2$ with a uniform distribution within the 1.5 μm thick nanocrystalline diamond film made from a microwave plasma with mixture of 4 vol% CH$_4$ and 96 vol% N$_2$ in the reactant gas. The density scale is established using relative sensitivity factors derived from implantation standards, and $1.8×10^{23}$ atoms/cm$^2$ 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 CH$_4$/N$_2$ 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 (CH$_4$) used in the reactant gas. Oxygen ($^{16}$O$^-$) has also been observed as an impurity in the film, which may be due to the Si substrate containing some SiO$_2$ at the surface even after the mechanical polishing with diamond powder. Figure 1(b) shows SIMS depth profiles of nitrogen ($^{14}$CN$^-$), hydrogen ($^1$H$^-$), oxygen ($^{16}$O$^-$), silicon
(28Si\(^{-}\)), 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 \(\times 10^{19}\) atoms/cm\(^3\)) being incorporated in the nanocrystalline diamond film during the deposition processing. Notice that the \(^{13}\text{C}^{-}\) 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\(_4\)/Ar discharge, demonstrating a relatively low density of nitrogen impurity (1.2 \(\times 10^{19}\) atoms/cm\(^3\)) being incorporated in the nanocrystalline diamond film during the deposition processing. Notice that the \(^{13}\text{C}^{-}\) 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.

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 diamond thin films versus concentration of N\(_2\) in the reactant gases used for CVD process.

![SIMS depth profile of nitrogen (26\(^{12}\text{C}^{-}\)), oxygen (16\(^{16}\text{O}^{-}\)), silicon (28\(^{28}\text{Si}^{-}\)), and carbon (12\(^{12}\text{C}^{-}\)) in the nanocrystalline diamond film prepared from a CH\(_4\)/N\(_2\) discharge; and (b) depth profile of nitrogen (26\(^{12}\text{C}^{-}\)), oxygen (16\(^{16}\text{O}^{-}\)), silicon (28\(^{28}\text{Si}^{-}\)), and carbon (12\(^{12}\text{C}^{-}\)) in nanocrystalline diamond produced from a CH\(_4\)/Ar discharge.](image1)

![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.](image2)
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 $5 \times 10^{13}$ atoms/cm$^2$ 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 $^7$Li, $^{23}$Na, and $^{39}$K from the standard ion-implanted sample, prepared by Charles Evans & Assoc., in which these three elements 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 from (a) CH$_4$/Ar and (b) CH$_4$/N$_2$ microwave discharges. 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. 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. 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 $1.2 \times 10^{10}$ atoms/cm$^3$, which also can be the background due to $^{13}$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 $9.5 \times 10^{20}$ to 2.4 $\times 10^{20}$ atoms/cm$^3$. As the substrate temperature decreases from 900 to 400°C, the incorporated nitrogen in nanodiamond coatings is increased from $1.2 \times 10^{20}$ to 1.15 $\times 10^{21}$ atoms/cm$^3$.

SIMS analyses also demonstrate that the alkalali 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.