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Field emission properties of two-layer structured SiCN films

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Abstract

The electron emission characteristics of two-layer structured silicon carbon nitride (SiCN) films, which were composed of amorphous and nanocrystalline phases, were studied. Rutherford backscattering spectroscopy (RBS) was used to determine the composition of the SiCN film. The ratio (Si;C)/N of the SiCN film was kept at approximately 0.75, which is identical to that of Si_3N_4 film. High resolution X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy were used to investigate the bonding structures of the SiCN films. In comparison with silicon nitride films, the turn-on voltage (for an emission current of 0.01 mA/cm^2) of the SiCN films was lower and the emission current densities of the SiCN significantly enhanced. The promising emission properties of the SiCN film could be due to the unique two-layer structure wherein nanocrystalline SiCN was grown on top of the amorphous interlayer with sp^2 CN bond in the SiCN film. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electron emission; SiCN; Nanocrystalline; Two-layer structure

1. Introduction

With the developments of vacuum microelectronic devices and flat panel displays, it becomes more and more important to acquire new cathode materials with high emission current at low electric fields. In the recent years, great interest has been focused on the electron field emission from carbon-based materials, such as diamond [1], diamond-like carbon [2], carbon nanotubes [3], etc. Diamond is expected to be well suited for application in microelectronics due to its negative electron affinity (NEA) and chemical inertness. However, because dia mond is a wide bandgap material and its shallow n-type doping is unsuccessful yet, electron transfer from the back electrode to the diamond surface is the determinant factor for electron field emission. The same issue also applied in the case of diamond-like carbon. Therefore, a few efforts have been reported in developing composite carbon-based thin films to solve the conductivity issue for electron field emission. Geis et al. [4,5] demonstrated that electron emission from diamond was determined by the electrical back contacts. Once increasing carrier injection into the conduction band of diamond, e.g. by roughing the electrode surface to result in internal field emission, electrons can then be easily emitted into vacuum due to diamond's NEA property. Amaratunga et al. [6] reported that a composite film containing carbon nanoparticles within an a-C:N matrix was comparable with carbon nanotubes in terms of field emission. The current transport through the film was suggested to take place by Zener-type Ohmic junction formed between the carbon nanoparticles and the semiconductor a-C:N matrix.

Recently, polycrystalline silicon carbon nitride films

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Table 1
Typical deposition conditions of the SiCN films for ECR-CVD

Source	$H_2 + N_2 + CH_3NH_2 + SiH_4$
$[H_2]:[N_2]:[CH_3NH_2]:[SiH_4]$ (sccm)	2.5:2.5:1 ~ 1.5:0.2 ~ 0.5
Microwave power (W)	1200
Total pressure (Pa)	0.4–0.65
Substrate temperature (°C)	550–800

have been successfully synthesized using chemical vapor deposition methods [7–12]. The new material has many remarkable properties such as wide bandgap [8,10], and high hardness [9,11]. In this paper, we report the field emission properties of two-layer structured SiCN films deposited by electron cyclotron resonance plasma chemical vapor deposition (ECR-CVD) system. It was thought worthwhile to investigate the field emission properties of the SiCN compounds due to the following two notable advantages. First, an amorphous SiCN phase has been shown to possess ultra-high oxidation resistance up to 1600°C [13]. Furthermore, the wide bandgap property of SiCN compound is quite similar to that of diamond [14] and may exhibit very low or even negative electron affinity (NEA). Recently, field emission measurements from quasi-aligned nanorods indicated a low turn-on field and high emission current [15], presumably due to their sharp geometric features which gave large field enhancement. It is thus of significant interest to investigate the field emission properties of the same SiCN material in film form without striking field enhancement. The two-layer structured SiCN films reported here were composed of amorphous and nanocrystalline phases. Combining the characteristics of nanocrystalline SiCN on the top and sp^2 CN bonds within the amorphous interlayer in the two-layer structured film, the SiCN film was demonstrated to exhibit promising field emission properties.

2. Experiments

The SiCN films were deposited in an ECR-CVD reactor. Details of the setup have been described elsewhere [10]. A 1.5-kW Astex AX2115 microwave source and an AX4400 electromagnet were employed to generate the ECR plasma as nitrogen or hydrogen was introduced into the reactor from the top shower ring right below the quartz window. The base pressure of the reactor was 1.3×10^{-4} Pa evacuated by a turbo molecular pump. The substrate stage was equipped with a BN heater for independent control of the substrate temperature. A thermocouple placed underneath the substrate holder was used to monitor the holder temperature. The silicon substrates were pre-cleaned using a H_2 ECR plasma before deposition. During deposition, two mixed streams of semiconductor grade H_2/N_2 and CH_3NH_2/SiH_4 were introduced into the reactor from the top shower ring and the shower ring above the substrate holder, respectively. Typical experimental conditions are presented in Table 1.

Field emission characterization was carried out using standard I–V measurements at a base pressure of 2.7×10^{-5} Pa. A Keithley 237 electrometer was employed for sourcing the voltage and measuring the current [16]. The measurement was performed by applying a positive voltage on a plane graphite electrode, which was placed 30 μm above the sample, and by collecting electrons emitted from the sample. Precaution is required to clean the sample before measurement in order to eliminate dust particle on the surface, which might cause false emission current signals. The pre-cleaning procedures consist of elimination of particles by blowing with a high-pressure N_2 gun and subsequent ultrasonic agitation in acetone for over 1 h. Stressing of the samples at constant voltage was also performed to study the emission stability of the sample.

3. Results and discussion

Fig. 1a shows the typical surface morphology of the SiCN film deposited by ECR plasma CVD. It reveals that there are two phases within the SiCN film: the aggregation of tiny crystals surrounded by an amorphous matrix. Further structural analysis was performed by high-resolution transmission electron microscopy (HRTEM). The HRTEM cross-sectional image of the SiCN film is shown in Fig. 1b. The HRTEM image confirms that the film deposited using $CH_3NH_2/SiH_4/N_2/H_2$ is composed of nanocrystalline and amorphous phases. The nanocrystalline film was grown on an amorphous interlayer which was several tens nanometer thick. A possible mechanism of the two-layer structure is that the nanocrystals are formed by the strain induced after a certain critical thickness of the amorphous film.

The composition of the SiCN films determined by Rutherford backscattering spectroscopy (RBS) shows that the ratio (Si;C)/N of the SiCN films was constant at approximately 0.75. That is, the ternary SiCN film possesses an N content similar to that of a binary Si_3N_4 film. In addition, there is no detectable compositional difference between the crystalline and the amorphous

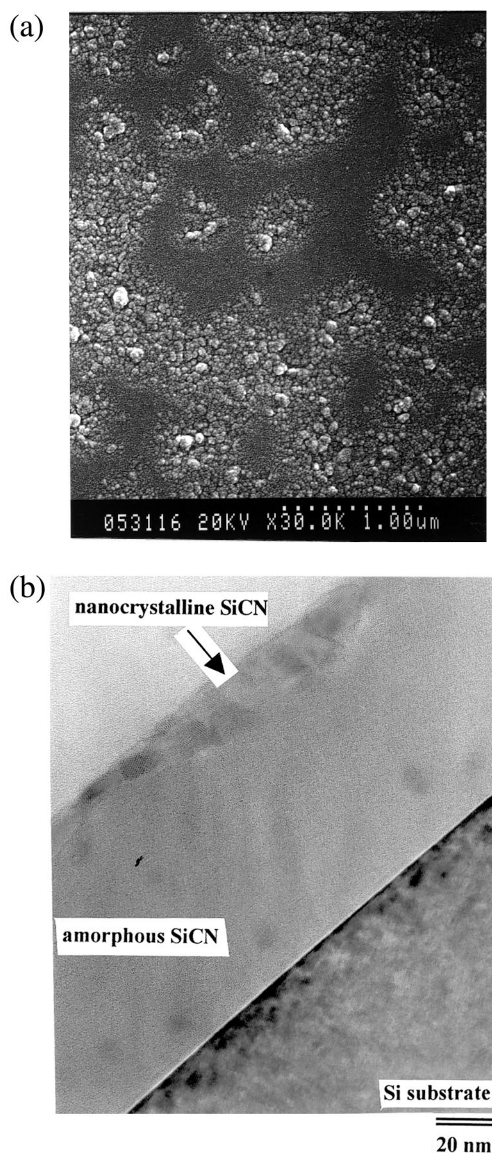

Fig. 1. (a) The SEM micrograph of the SiCN film deposited by ECR CVD. (b) The cross-sectional TEM image of the SiCN film.

phases. The silicon to carbon ratio within the film depends on the inlet gas ratio of $[CH_3NH_2]/[SiH_4]$ [12].

The chemical bonding states of the SiCN film were investigated by X-ray photo-electron spectroscopy (XPS) and Raman spectroscopy. Typical high resolution XPS scans of the Si(2p), C(1s), and N(1s) peaks are shown in Fig. 2. The C(1s) photo-electron peak is composed of three components centered at 284.4, 285.9 eV and 288.1 eV, whereas the N(1s) peak consists of two components centered at 398.4 and 399.8 eV. While numerous papers have reported XPS measurements of binary CN_x films [17–21], there is no definite conclusion of the assignments of the C and N subpeaks. However, according to the tentative assignments by Tabbal et al. [22] and Stoner et al. [23], the subpeaks we observed are attributed to C bonded to C in the layers, sp^2 trigonal CN bonding, C–O bonds, N–Si bonds and N bonded to an sp^2-hybridized C, respectively. The C–C and C–O peaks disappeared after sputtering with Ar^+ ions, indicating that C–C and C–O bondings were associated with contamination on the surface. The Si(2p) photo-electron peak could not be resolved into more than one peak. The peak centered at 102.6 eV was assigned to Si–N bonding. Notably, there are no major peaks that match the C–Si binding energy of 282.8 eV and the Si–C binding energy of 100.3 eV, thus suggesting the absence of Si–C bonds in the material. The sp^2-hybridized C within the SiCN film was further confirmed by Raman measurement. The Raman spectra of the SiCN and silicon nitride films are shown in Fig. 3. The Raman spectrum of the SiCN film shows two broad peaks at approximately 1200–1600 cm^{-1}, which corresponded to D and G bands of sp^2-carbon, whereas that of the binary Si_3N_4 does not give any signal in this region. The presence of this pronounced Raman band indicates carbon π bond within the SiCN film [24], which is consistent with the XPS results of sp^2 CN bonding appearance.

Typical field-emission characteristics of the as-deposited SiCN films, emission current density J as a function of applied field E, are shown in Fig. 4. The emission current densities were calculated from the

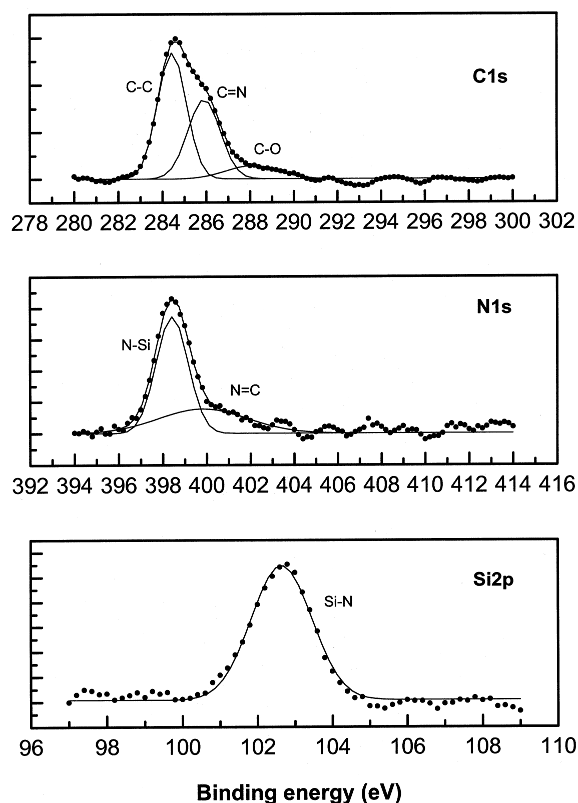

Fig. 2. Typical XPS spectra of N(1s), Si(2p) and C(1s) taken from the SiCN film.

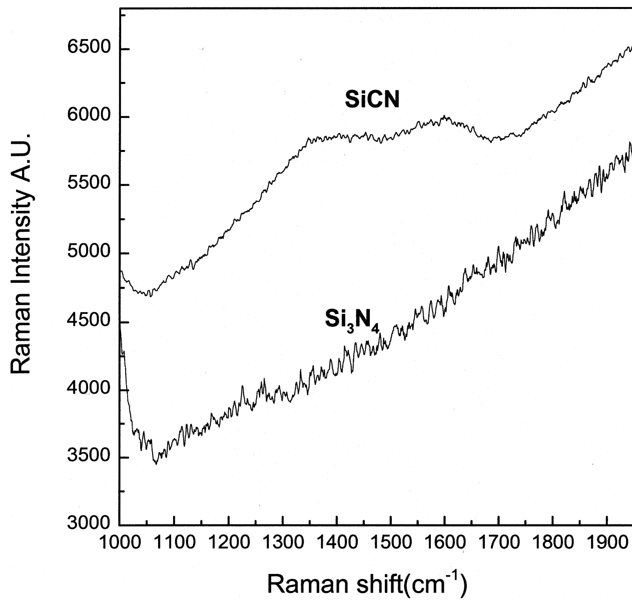

Fig. 3. Typical Raman spectra of the SiCN film and Si_3N_4 film.

measured current dividing by the sample area assuming homogeneous electron emission from the entire sample. The turn-on field, which is defined as the applied field required to draw a field-emission current density of 0.01 mA /cm^2 [25], of a SiCN film with composition ratio [C]:[Si]:[N] of 22:21:57 was 18 V/μm, and the maximum current density at 36.7 V/μm was 0.7 mA/cm^2. Oscillations in the I–V curves were observed at high fields. This is likely due to the presence of predominant emission sites (e.g. some crystalline structures) which are burned one after the other. However, the origins of signal oscillation of the SiCN film that occurred at high applied fields are still unclear. A similar characteristic was also observed for the electron emission from nanostructured carbon films [26]. The inset of Fig. 4 shows the Fowler–Nordheim (FN) plot of the I–V characteristic of the film. It seems that the emission curve of the SiCN film did not follow the FN behavior. For comparison, the I–V measurement of a silicon nitride film, which was also deposited by ECR plasma CVD without CH_3NH_2 addition, is also shown in Fig. 4. It should be noted that the silicon nitride film grown in this study also exhibited a two-layer structure [12] similar to that of the SiCN film. As shown in Fig. 4, the turn-on field of the Si_3N_4 film was 30 V/μm and the maximum current density at 36.7 V/μm was only 30 μA /cm^2. It shows that the field emission properties

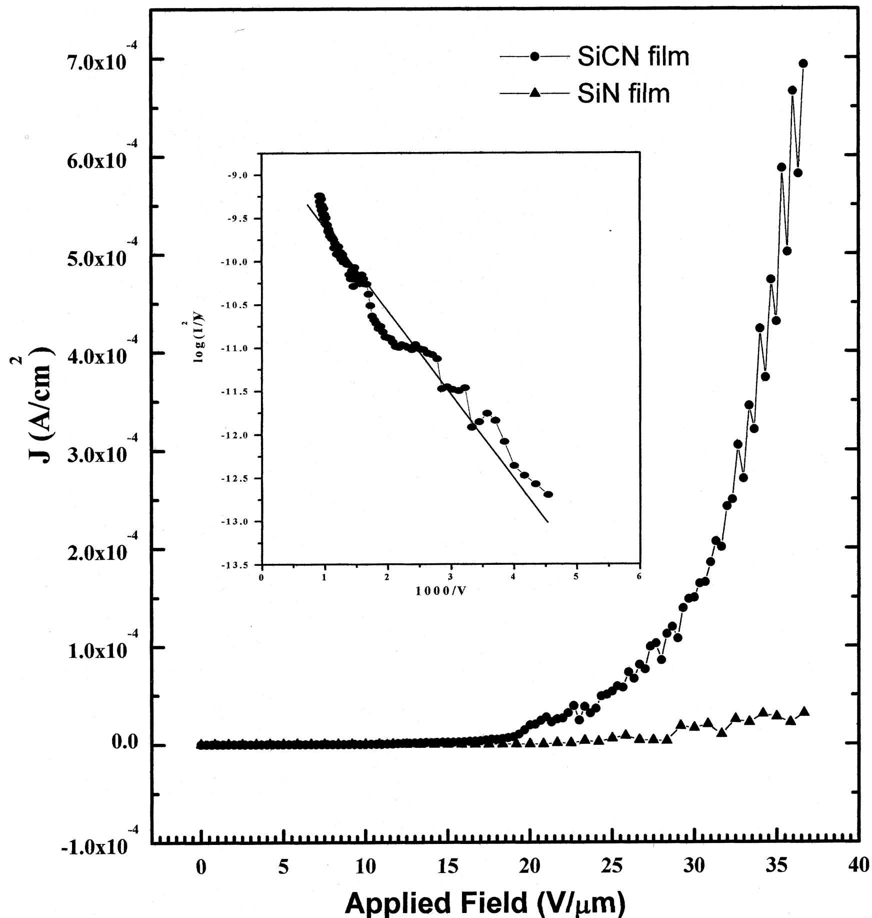

Fig. 4. Field emission J–E curves of the SiCN and SiN. The inset shows the F–N plot of the SiCN film.

of Si_3N_4 is poorer than that of the SiCN film but is comparable to ordinary silicon or diamond films.

The rather promising electron emission properties of the two-layer structured SiN film could be contributed to the SiN nanocrystals of the top layer. Crystalline Si_3N_4 has a wide bandgap of 4.7 eV [27]. While it is not clear whether Si_3N_4 could have NEA or a low electron affinity reported for other wide band gap materials [28–30], pure Si_3N_4 films should exhibit quite poor emission characteristics due to their insulating property. Hence, we suggest that the addition of nanocrystalline Si_3N_4 could provide either a rougher surface to enhance local electric fields or a low electron affinity surface to lower the barrier for electron emission, resulting in the promising electron emission properties. Moreover, a significant reduction of the turn-on voltage from 30 V/μm to 18 V/μm and pronounced enhancement in the emission current density were observed in the case of carbon incorporation within the films. As concluded by Geis et al. [4,5] and Schlesser et al. [31], for electron field emission not only the surface condition is important, but also the conducting path for electrons from the back electrode to the surface is crucial. It has been demonstrated that the conductivity of diamond-like-carbon [32]and tetrahedral amorphous carbon [33] films can be increased as a proper concentration of nitrogen is incorporated to form sp^2 CN bonding within the carbon sp^3 films. The SiCN film deposited by ECR plasma CVD also possesses sp^2 CN bonds as the XPS and Raman results indicated. In contrast to silicon nitride film, wherein electron conduction is limited by its insulating property, the amorphous SiCN interlayer between silicon substrate and nanocrystalline SiCN film could play the role of electron transfer medium. Therefore, the turn-on voltage is decreased and the emission current densities of the SiCN enhanced pronouncedly. Combining the characteristics of nanocrystalline SiCN on the top and sp^2 CN bonds within the amorphous interlayer in the two-layer structured film, the SiCN film deposited using $CH_3NH_2/SiH_4/N_2/H_2$ in an ECR plasma CVD reactor was demonstrated to exhibit promising field emission properties.

For practical application, it is important to investigate the long time stability of the material to be used in field emission devices. Fig. 5 depicts the emission current variation of SiCN film at an applied voltage of 25.3 V/μm for 9 h. In the initial period, the voltage is swept from 0 V/μm to 25.3 V/μm at which the current density is 10 times higher than turn-on field (0.01 mA/cm^2), with a ramp rate at 20 V/min. As shown in Fig. 5, the emission current is kept at an average level of 0.1 mA/cm^2 after 80 min. The emission stability of the two-layer structured SiCN film is superior to that of carbon nanotubes (CNT) [16] or carbon-coated-Si microtips [34].

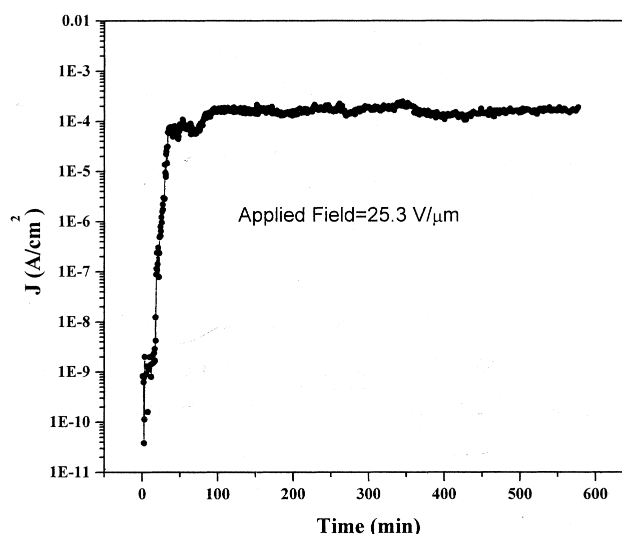

Fig. 5. The long-time stability of SiCN film.

4. Conclusions

In conclusion, the electron emission characteristics of silicon carbon nitride films deposited using $CH_3NH_2/SiH_4/N_2/H_2$ were demonstrated to possess promising field emission properties. In comparison with silicon nitride films, the turn-on voltage of the SiCN film was lower and the emission current density of the SiCN was enhanced pronouncedly. The promising emission properties of the SiCN film could be due to the unique two-layer structure wherein nanocrystalline SiCN was grown on top of the amorphous interlayer with sp^2 CN bond in the SiCN film.

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