Liquid phase deposition of amorphous carbon (a-C) and carbon nitride (CNx) film has been attempted by means of electrolysis of organic liquids. The deposition of a-C film is achieved by applying a DC bias voltage to substrate immersed in methanol. Smooth and homogeneous a-C films are deposited on specific substrate materials such as Si, Ti, and Al. The deposition of CNx films is carried out by using nitrogen-containing electrolyte such as acrylonitrile (CH$_2$CHCN). Continuous and uniform films are obtained with the application of both negative and positive bias voltages. The atomic ratios of nitrogen to carbon in the grown films are estimated as 0.16–0.28.

Those results demonstrate the feasibility of using liquid deposition techniques for the production of carbon related materials. [DOI: 10.1380/ejssnt.2009.102]

Keywords: Carbon; Amorphous thin films; Electrochemical methods; Growth; Field emission; Carbon nitride

I. INTRODUCTION

The fabrication of carbon related materials such as diamond, carbon nanotube, and amorphous carbon has been studied extensively by conventional vapor deposition techniques such as chemical vapor deposition, reactive sputtering, and pulse laser deposition. In this work, liquid phase deposition of amorphous carbon (a-C) and carbon nitride (CNx) is proposed to develop alternative techniques for fabrication of carbon related materials. The liquid deposition technique offers numerous advantages over conventional vapor deposition techniques: simplicity of the experimental apparatus, low growth temperature, and scalability of the deposition area. Therefore, it is worthwhile examining the feasibility of using liquid deposition for the production of carbon related materials.

The electrochemical deposition of a-C films has been attempted by using organic liquids such as ethanol, methanol, and N,N-dimethyl formamide [1–3]. We have studied field emission properties of a-C films grown by the liquid deposition technique using methanol as an electrolyte [4]. The deposition of a-C films was achieved by applying a DC bias voltage to the substrate immersed in methanol. Our previous work demonstrated that a-C films were successfully grown on Si substrates [4]. In this work, we carried out the deposition of a-C films on various substrates, which are expected to improve effects of back contact between the substrate and a-C film. The emission current density for a-C films grown on different substrates is measured as a function of the applied field.

In addition, we have attempted the liquid deposition of CNx films by means of electrolytic system using acrylonitrile (CH$_2$CHCN). Since the theoretical prediction of the tetrahedral β-C$_3$N$_4$ phase by Liu and Cohen [5], carbon nitride has attracted much attention as a transparent hard coating and as a wide-bandgap semiconductor [6]. Initial attempts to fabricate carbon nitride films using nitrogen-containing organic liquids such as acetonitrile and acrylonitrile were reported by Wang et al [7, 8]. Their results suggest the feasibility of carbon nitride formation using a nitrogen-containing liquid. However, the grown film has an amorphous structure with nitrogen content lower than that of the β-C$_3$N$_4$ phase. The fundamental properties of the grown films such as composition, structure, and bonding states should be clarified to improve the growth process of carbon nitride films. The deposition of CNx films are achieved by the application of DC bias voltage to substrates immersed in acrylonitrile. The polarity and strength of the bias voltage are important parameters for film growth because charged species are electrically attracted to the substrate through the application of the bias voltage. We carefully examined the effects of the deposition parameters such as the polarity and strength of the bias voltage on the properties of the grown films.

II. EXPERIMENTAL PROCEDURE

Liquid phase deposition of a-C and CNx films was carried out by applying a DC bias voltage to the substrate immersed in organic liquid. Figure 1 shows the apparatus used for deposition; it consists of a glass vessel, two elec-
Field emission from the grown film was measured using a parallel plate configuration by using indium-tin oxide (ITO) coated glass plate as an anode. Contact electrode was formed on the back side of Si substrate. During measurements, the vacuum chamber was maintained at 2 × 10^{-5} \text{ Pa} using a molecular-turbomolecular pumping system. The DC voltage of up to +10 kV was applied onto the ITO anode to cause electron emission from the samples. The emission current was recorded to plot the current density \( J \) as a function of the applied electric field \( E \).

Nitrogen-containing organic liquid such as acrylonitrile (CH\(_2\)CN) was used for the deposition of a-C films. To clarify the fundamental properties of the grown films, their surface morphology, compositions, bonding states, and structures were characterized by Scanning electron microscopy (SEM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS).

### III. RESULTS AND DISCUSSION

#### A. Deposition of amorphous carbon films

Among various substrates used for deposition, it was found that the films grow effectively on specific substrates such as Si, Ti and Al when the negative bias voltage was applied to the substrates. Figures 2(a) and 2(b) respectively show SEM images of films grown on Ti and Al. Previously, we have reported that a-C films grown on an n-Si (100) substrate have smooth and homogeneous surface morphology [1]. Figure 2(a) shows that the film grown on Ti has a smooth surface similar to that of the a-C film grown on Si substrate. In contrast, some craters and rough area are visible on the film grown on Al. Those craters are probably caused by the intense DC field, which peels the Al layer from the Si substrate during deposition.

Figures 3(a) and 3(b) show Raman spectra of the films grown on Ti and Al, respectively. The Raman spectra of the grown films indicate two broad peaks around 1560 cm\(^{-1}\) and 1350 cm\(^{-1}\), which are respectively referred to as G peak and D peak. Features of these peaks are commonly observed in the Raman spectra of a-C films grown using conventional vapor deposition techniques [9]. The D peak arises from clustering sp\(^2\) carbon phase into aromatic rings, whereas the G peak arises from the all sp\(^2\) phase with both chain and ring configurations [10]. Therefore, the intensity ratio of the D peak to the G peak, \( I(D)/I(G) \), suggests the degree of clustering of the sp\(^2\) carbon phase. Ferrari and Robertson have shown a quantitative relationship between the intensity ratio \( I(D)/I(G) \) and the size of the sp\(^2\)-carbon cluster [11]. By applying their relationship to our results, the cluster size of a-C films grown on both Si and Ti substrates can be estimated to be 1.5 nm or less. On the other hand, the size of the sp\(^2\) cluster in a-C film grown on Al can be estimated to be approximately 1.1 nm. Furthermore, an upward shift of the G peak to 1600 cm\(^{-1}\) is observed in the Raman spectra of a-C film grown on Al. Such a shift of the G peaks to a higher wave number is probably attributed to the hydrogenation of the a-C film or the reduction in the sp\(^3\)-carbon phase. These results suggest that characteristics of the internal structures, such as the sp\(^2\) cluster size, vary according to the substrate materials that are used in our liquid deposition system.

The field emission properties of a-C films grown on Si and Ti were measured to evaluate the feasibility of liquid-deposited a-C films for practical use in field emitters. From almost all samples, emission current higher than 10 \( \mu \text{A/cm}^2 \) was observed under an applied electric field lower than 5 V/\( \mu \text{m} \). The “forming” process that is commonly performed to achieve the stable emission current is not required for their samples. Figures 4(a) and 4(b) show typical \( J–E \) characteristics obtained from the a-C films grown on Si and Ti, respectively. We define the threshold field as the electric field that is required to generate
FIG. 3: Raman spectra of a-C films grown on (a) Ti and (b) Al.

FIG. 4: Field emission $J - V$ characteristics of a-C films grown on (a) Si and (b) Ti.

the emission current larger than 1 $\mu$A/cm$^2$. In Fig. 4, the $J - E$ plots indicate the threshold fields as low as 4.4 V/µm and 4.8 V/µm for a-C/Si and a-C/Ti, respectively. In this work, most of the samples show the threshold fields in the range of 3-5 V/µm, which are almost independent of the substrate materials. Furthermore, a few samples show the threshold fields as low as 1 V/µm although features of their samples are similar to others. Threshold fields of undoped a-C and diamond films were reported as 10-20 V/µm [12–17]. This threshold field obtained in this work is the lowest ever reported for undoped a-C films. It is noteworthy that neither a high-vacuum system nor a high-power rf generator is necessary for the production of such excellent emitter materials.

The mechanism of electron emission at the low threshold should be discussed to improve the emission properties of the a-C film. From Raman spectra shown in Fig. 3, the $sp^2$ cluster size was estimated to be 1.5 nm or less; this dimension is equivalent to the diameter of a single-walled carbon nanotube. Because $sp^2$ carbon clusters have conductive and dielectric properties that differ from those of $sp^3$-rich region, it is suggested that lines of electric force are focused locally on $sp^2$ carbon phase embedded in the a-C film. Therefore, we can conclude that $sp^2$ carbon clusters of the a-C film are attributed to strong field enhancement that is comparable to those of carbon nanotubes.

As shown Fig. 4, the $J - V$ characteristic of a-C/Si shows a saturation of the current density under a high applied field. On the other hand, emission properties of a-C/Ti show weak saturation behavior: the emission properties are improved by forming Ti interfacial layer. In this case, the current saturation can be explained in terms of potential barrier at a-C/Si interface. It is known that Ti is a strong carbide-forming metal and utilized to form Ohmic contacts onto diamond surface [18]. Therefore, the formation of TiC layer at the interface reduces the contact resistance and improves the emission properties under a high applied field.

B. Deposition of carbon nitride films

Continuous and uniform films were deposited on Si substrates through the application of a bias voltage between the electrodes immersed in acrylonitrile liquid. Previously, it was reported that a-CN$_x$ films were deposited electrochemically using acrylonitrile, provided that a positive bias voltage was applied to the substrates [8]. The results of this study showed that continuous and uniform films were also grown by the application of a negative bias voltage to the substrates. The growth rates of the films are between 100-200 nm/h; they depend on deposition parameters such as the strength and polarity of the bias voltage applied to the substrate. In particular, the growth rate decreases gradually with reduced bias voltage during film growth. The thickness of films grown with a negative bias voltage tends to be less than that of films grown with a positive bias voltage. Figures 5(a) and 5(b) respectively show typical SEM images of films grown by the application of negative and positive bias voltages. The film grown with the negative bias voltage shows a smooth and uniform surface; it consists of compact grains. In contrast, a rough and uneven surface is visible in the case of the film grown with the positive bias voltage. These differences in the surface morphology of the films suggest that the bias voltage polarity strongly influences the growth mechanism and fundamental properties of the films.

We carried out XPS measurements to evaluate the compositions and bonding states of the grown films. Figure 6 shows XPS survey spectra for a film grown with a bias voltage of $−5$ kV and at a liquid temperature of 70 °C. Figure 6 (a) shows that the spectrum of the as-grown sample has distinct peaks attributable to C 1s, N 1s, and O 1s at 286, 399, and 532 eV, respectively. Small peaks are also visible at around 100 and 150 eV in the spectrum; these peaks are respectively attributed to Si 2p and Si 2s electrons, which are detected from the substrates.
The oxygen and nitrogen detected from the as-grown film might be localized in the vicinity of the surface because the presence of oxygen is often observed as surface contamination caused by the exposure of samples to the atmosphere. We also conducted XPS measurements after Ar ion etching of the as-grown film to reduce the surface contamination. Figure 6(b) shows that both O 1s and N 1s peaks are found in the spectrum of the sample, even after Ar ion etching. Therefore, the XPS spectra revealed the presence of C, N, and O as major components of the grown films. The atomic ratios of nitrogen to carbon (N/C) are determined as 0.16-0.28, which are comparable to those of carbon nitride films formed by conventional vapor deposition techniques. From analyses of the C 1s and N 1s spectra, the major bonding states of the films grown using acrylonitrile were attributed to a mixture of C≡N and hydrogenated C=N bonds. On the other hand, the grown films contain a large amount of oxygen, although no oxygen exists in the acrylonitrile molecule (CH$_2$CHCN). We speculate that the oxygen incorporation into the film is attributable to residual H$_2$O or O$_2$ dissolved in the liquid.

Raman spectra of CN$_x$ films show two broad peaks at 1580 cm$^{-1}$ and 1320 cm$^{-1}$, which are designated respectively as G and D peaks. These peaks are also observed in the spectra of liquid-deposited a-C films using methanol as shown in Fig. 3. From the analysis based on intensity ratio of the D peak to the G peak, the size of the sp$^2$ cluster in CN$_x$ film was estimated as 1.7-2.0 nm. Figures 7(a) and 7(b) respectively show the sp$^2$ carbon cluster sizes as functions of nitrogen and oxygen concentrations. The correlation between the sp$^2$ cluster size and the nitrogen concentration in the grown films is apparent in Fig. 7(a); the cluster size increases with increasing nitrogen concentration. On the other hand, oxygen incorporation has less influence on the sp$^2$ cluster size, as shown in Fig. 7(b). Therefore, we conclude that increasing the nitrogen concentration enhances the graphitization of the films grown using acrylonitrile.

FIG. 6: XPS survey spectra of (a) as-grown and (b) Ar-ion etched sample.

FIG. 7: Size of sp$^2$ carbon cluster as functions of (a) nitrogen and (b) oxygen concentration for film grown with various deposition parameters.

IV. CONCLUSIONS

Liquid phase deposition of a-C film was achieved by applying a DC bias voltage to the substrates immersed in methanol. SEM and Raman results revealed that a-C films were deposited on specific substrate materials such as Si, Ti, and Al. In particular, the films grown on Si and Ti have smooth and homogeneous surfaces, so both films are suitable for field emitter applications. Field emission measurements showed excellent emission properties such as threshold fields lower than 5 V/µm.

The composition and bonding properties of carbon nitride films grown by the bias application to the substrates immersed in acrylonitrile were also studied. Continuous and uniform films were grown by the application of both negative and positive bias voltages. The XPS survey spectra revealed the presence of C, N, and O atoms as the major components of the grown films. The N/C ratios in the grown films were 0.16-0.28, which are comparable to those of a-CN$_x$ films fabricated by conventional vapor deposition techniques.

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