Paper

Deposition of Nitrogen Doped Carbon Film by Electrolysis of Methanol-Ammonia Solution

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Nitrogen doped carbon film has been grown on silicon substrate at temperature of 60 degrees in the methanol-ammonia solution. The substrate was negatively biased with a dc potential less than 100 V for current density of 4 mA/cm^2 as constant-current electrolysis. The work function and the resistivity of the film decreased remarkably. From the results of Raman spectra and X-ray photoelectron spectroscopy, it was also confirmed that the film is amorphous containing only small amounts of diamond component, and nitrogen atoms are doped in the film though containing some organic residue.

Keywords : solution growth, carbon, diamond-like carbon, field emission

1. Introduction

Diamond like carbon (DLC) films are generally prepared from the various gas phase methods, such as ion-beam sputtering, laser ablation deposition and chemical vapor deposition techniques [1]-[8]. Although high quality films and rapid growth rate have been achieved, the gas phase techniques require the substrate temperature to be at several hundred degrees centigrade. Reduction of the temperature will prevent damage of the low melting substrates, i.e., plastics, and it will also cause internal stress of the films. In addition, it is difficult to control the dopant quantity into the films using the above techniques.

There is experimental evidence that most materials can also be deposited in liquid phase using electrolysis techniques [9]-[14]. Namba and Wang et al attempted to grow DLC films in methanol solution at a temperature less than 60 degrees [9],[11]. Suzuki et al recently made an attempt to deposit carbon films by electrolysis of a water-ethylene glycol [10]. In these cases, however, the applied voltage during deposition kept at more than several kV and there were no reports on the deposited films in liquid phase techniques relating to applications in microelectronics and flat-panel displays.

In the present work, a film deposition was attempted in methanol-ammonia solution based on the techniques of electrolysis at the applied voltage less than 100 V. The work function of the film decreased markedly with regard to the one deposited in methanol solution. It was confirmed that the film is composed of diamond structure and amorphous carbon structure, and nitrogen atoms are doped in the film though containing some organic residue. These results have suggested that thus liquid phase techniques are useful for the doping system with various atoms in carbon film by the selection of a proper solution.

Moreover, we have also reported about the electron emission characteristics from the carbon films deposited in methanol and methanol-ammonia solutions.

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2. Experiments

A schematic diagram of the deposition system is shown in Fig. 1. The positive electrode used in the present experiment was a carbon plate (Φ20 mm×1 mm). An n-type silicon (100) substrate with resistivity of 10 Ωcm and a size of 20×30×0.3 mm^3 was mounted on the negative electrode. The substrate was cleaned in deionized water by ultrasonic treatment and then was dipped in an HF solution (5 wt%) for 10 min. The silicon substrate and the carbon plate were immersed into the methanol solution (99.5%) in a 200 ml beaker. The distance between the electrodes was set to 2 mm. Before deposition, ammonia gas was bubbled in the methanol solution with a flux of 3 l/min for 3 min. For compared with the deposition in methanol-ammonia solution, methanol solution without bubbling also was used as the electrolyte. The constant current flowed to the electrodes was 4 mA/cm^2 for 8 h under a constant temperature of 60 degrees.

The properties of the deposited films were investigated using

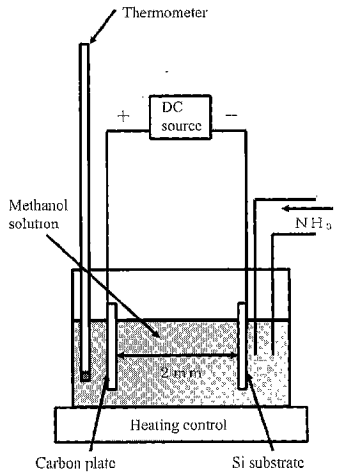


Fig. 1. Schematic diagram of deposition system

various experimental techniques. The work function of the film was measured in air using a Kelvin probe (FAC-1, Riken Keiki Co., Ltd). The morphology of the film was examined using atomic force microscopy (AFM: SPI-3800, Seiko Instruments Inc.). The crystal structure and chemical composition of the film were analyzed using a 244 nm UV Raman spectroscopy and X-ray photoelectron spectroscopy (XPS), respectively. For field electron emission from the film, the film was mounted as the cathode in a vacuum chamber with a base pressure of 1.9×10^{-6} Pa. A glass plate coated with indium tin oxide was placed 80 μm above the cathode as the anode using glass-fiber spacers. The emission current against the anode voltage was measured after the specimen was annealed for 2 h at 200 degrees in the above vacuum condition.

3. Results and Discussion

Figure 2 shows changes of the applied voltage with deposition time at 4 mA/cm^2 for methanol and methanol-ammonia solutions. In contrast to the deposition in the methanol solution, the applied voltage for the deposition in the methanol-ammonia solution was markedly lowered and it remained relatively constant during the deposition of 8 h, rising by about 18 V from the initial voltage.

Depending on the kinds of the solution, two types of films were deposited on the n-Si substrate. Film deposited in methanol was fragile and the average thickness of the film was about 2 μm. The resistivity and the work function of the film were 10^{14} Ωcm and 5.0 eV, respectively. In the case of the deposition in the methanol-ammonia, however, the obtained film was plastic and the average thickness of the film was about 800 nm. Furthermore, the resistivity and work function of the film decreased remarkably, and the values of those were 10^{8} Ωcm and 4.6 eV, respectively. It was reported by several authors that the resistivity and work function of the DLC film decreased by nitrogen doping because nitrogen acts as donor [5]-[7]. Therefore, the change of the work function and conductivity are considered to be due to nitrogen doping in the film deposited in methanol-ammonia solution.

Hence, the films were investigated to clarify the influence of the deposition solutions on the variation of the physical and chemical properties of the films. The roughness (Rz: mean value of 30 data) of about 0.8 μm on the film deposited in methanol was observed using AFM on 20 μm by 20 μm scans. The roughness of the film deposited in methanol-ammonia was about 300 nm.

Figure 3 shows the deconvoluted Raman spectra for the films deposited in different solutions. All the spectra obtained for the both films have three different composite structures, i.e., crystalline graphite at 1600 cm^{-1}, amorphous carbon at 1580 cm^{-1} (A-band) and DLC at around 1400 cm^{-1} (D-band) [1],[5],[8],[11],[15],[16]. Depending on the band of amorphous carbon, crystalline graphite and DLC components, furthermore, we note that: (I) the film deposited in methanol consists of a mixture of 50 % diamond and 50 % amorphous carbon components, (II) the film deposited in methanol-ammonia is amorphous carbon containing only small amounts of diamond components.

The deposited films were also examined by XPS. In C_{1s} spectra, a relatively sharper peak at 284.5 eV and a shoulder peak at around 287 eV were observed for the films deposited in methanol and methanol-ammonia solutions (data not shown). The energy of 284.5 eV agrees well with the binding energy of graphite peak [1],[9]. On the other hand, the energy of around 287 eV is considered to correspond to that of diamond peak [1],[9]. Taken together, these observations indicate that the both films are considered to be consisting of the some diamond phase.

The film deposited in methanol-ammonia was nitrogen-rich (11 atom%) compared to the film deposited in methanol. In N_{1s} spectra, moreover, a sharp-peak energy at 399 eV corresponds to the C-N and –CN bonds, was observed for the film. Since the film deposited in methanol-ammonia was plastic, however, these

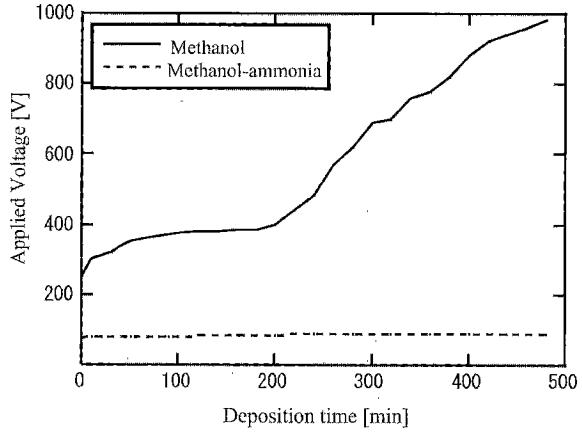
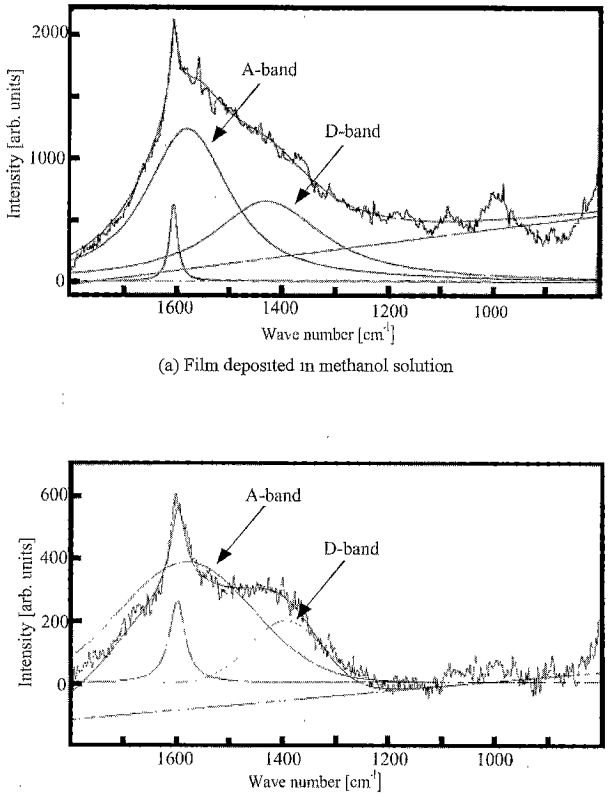


Fig. 2. Dependence of the applied voltage with deposition time for methanol-ammonia solutions



(a) Film deposited in methanol solution

(b) Film deposited in methanol-ammonia solution

Fig. 3. Raman spectra of films deposited for 8 h at 4 mA/cm^2 in (a) methanol and (b) methanol-ammonia solutions

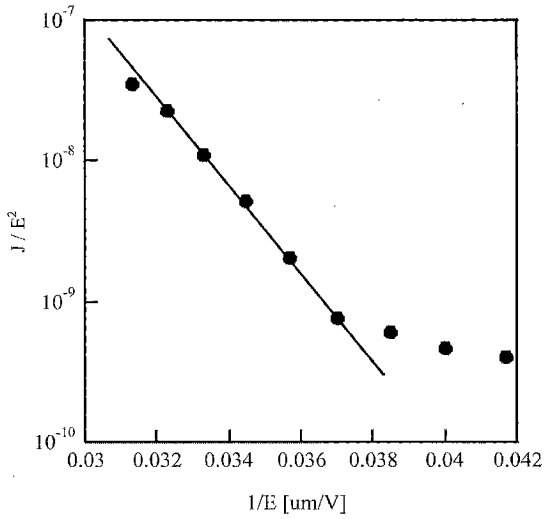


Fig. 4. Fowler-Nordheim plot of film deposited in methanol solution

results suggest that the film is contained some organic residue resulting from a reaction of ammonia and methanol, in addition to nitrogen doping in the film.

On the other hand, the emission current against the anode voltage was measured for the films deposited in methanol and methanol-ammonia solutions. The threshold field from the deposited in methanol was less than 20 V・μm^{-1}, indicating to stand comparison with that of the films using gas phase techniques [2],[7]. Figure 4 shows the emission characteristic plotted in conventional Fowler-Nordheim (FN) form for the film deposited in methanol. The FN plot is straight line over a significant portion of the field range, although there seems some indication that a different emission region may exist below about 27 V・μm^{-1} in this case. The effective barrier height for emission formally calculated from the FN plot was found to be 0.128 eV. The surface morphology of the film indicated that the film surface is not flat and the roughness is about 0.8 μm on average. The emission is more likely to be a significant particular sites rather than over the entire surface [4],[8]. There seems to be the enhancement factor such as the surface roughness on the film with respect to the emission phenomenon. Therefore, this very low barrier height value could be ascribed either to specific electronic properties of the DLC material itself, or to strong electric field inhomogeneity such as field enhancement on sharp protrusions. On the other hand, the field emission from the film deposited in methanol-ammonia was not observed. Thus difference in the emission properties is considered that the high nitrogen content and organic contaminants suppress electron emission from the film [5]. However, further studies are needed for confirmation of this hypothesis.

4. Conclusions

Nitrogen carbon film was grown on n-type silicon substrate at temperature of 60 degrees in the methanol-ammonia solution. The effect of nitrogen doping on the electronic and chemical properties of carbon film was characterized. From the results of Raman spectra, it was confirmed that the film is amorphous carbon containing only small amounts of diamond components. Moreover, the resistivity and work function of the film decreased remarkably with regard to that of film deposited in methanol solution. The variation of conductivity and work function for the film deposited in methanol-ammonia suggests that nitrogen acts as donor. Since the film was plastic, however, it is considered that the film is contained some organic residue resulting from a reaction of ammonia and methanol. On the other hand, the field emission from the film was not observed in contrast to the film deposited in methanol solution. Thus difference in the emission properties is considered that the high nitrogen content and the organic contaminants, suppress electron emission from the film. Taking all the factors into consideration, we propose that thus liquid phase techniques are useful for the doping system with various atoms in carbon film by the selection of a proper solution.

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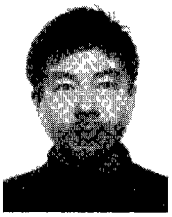

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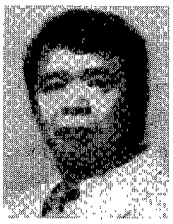

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