한국전기전자재료학회 2006년도 영호남 합동 학술대회 및 센서박막
재료연구회 / 기술교육위원회 춘계학술대회 논문집 (2006. 5. 19)

GROWTH OF AMORPHOUS CARBON THIN FILMS BY RF PLASMA CVD

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Abstract

In this paper, the author describes a-C films grown in pure methane plasma without any diluent gas by using RF plasma-enhanced CVD, and the variations in their structural features and surface morphologies are examined as a function of substrate temperature. Raman spectroscopy and scanning electron microscopy were performed to characterize the properties of the film.

Key Words : amorphous Carbon, CVD, FED, SEM

1. Introduction

In recent years, there have been numerous reports on various applications using carbon-based materials such as diamond films, amorphous carbon (a-C) films, and carbon nanotubes [1-6]. Generally, diamond films have been deposited on substrates by chemical vapor deposition (CVD) while introducing a hydrocarbon gas diluted with a certain amount of hydrogen gas. Here, the hydrogen inhibits the growth of graphite or a-C and maintains the sp3 surface structure by various mechanisms [7, 8]. Several articles have reported on the influence of the gaseous mixture ratio on the properties of carbon films deposited by CVD [9, 10]. For example, diamond samples were prepared by microwave plasma enhanced CVD at 0.3%"'0.8% methane gas in hydrogen gas [9]. On the other hand, a-C thin films were deposited in the gaseous mixture of 90% Ar : 10% CH_4 by RF plasma-enhanced CVD [11]. a-C thin films can be reproducibly deposited at a high deposition rate at low temperature over a large area, and they have shown low field electron emission. However, a limited number of reports have discussed a-C films grown in a pure methane gas without any diluent gas.

In this paper, the author describes a-C films grown in pure methane plasma without any diluent gas by using RF plasma-enhanced CVD, and the variations in their structural features and surface morphologies are examined as a function of substrate temperature. Raman spectroscopy and scanning electron microscopy were performed to characterize the properties of the film.

2. Experimental

Table 1 Synthesis conditions of a-C thin films grown by RF plasma-enhanced CVD.

Substrate : P doped n-type Si(100)
Source gas : CH_4 (10sccm)
Base pressure : 1×10^{-3} (Pa)
Gas pressure : 7 (Pa)
RF power : 100 (W) Constant
Substrate temp. : RT ~ 800℃
Thickness : ~2000Å

An RF plasma-enhanced CVD system was used to grow a-C films. The CVD conditions are summarized in Table 1.

3. Results and discussions

Figure 1 (a), (b), (c) and (d) show SEM images of the samples prepared at substrate temperatures of RT, 500℃, 600℃and 800℃respectively. SEM morphology of CVD a-C films changed with an increase in substrate temperature, but the same kind of surface morphology shown in Figure 1 (c) and (d) were observed over 60 0℃. In the sample prepared at a substrate temperature of 600", a curvilinear or concave morphology appeared on the surface and created a network [12]. This shape is similar with the CVD graphite film prepared by A.N. Obraztsov et al. [13] and has a high field enhancement factor that depends on the emitter geometry.

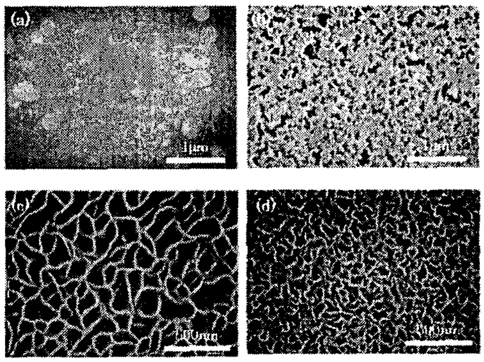

Fig. 1 SEM images of a-C films grown at: (a) RT, (b) 50℃0; (c) 60℃0; (d) 800℃

The density of the mesh on the network increased with increasing substrate temperature as shown in Figure 1 (c) and (d).

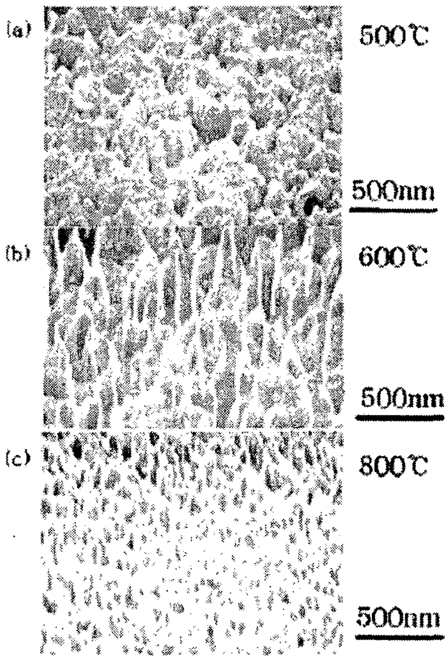

Fig. 2 45°tilt angle SEM images of a-C films grown at: (a) 500℃; (b) 60℃0; (c) 800℃

Figure 2 (a), (b), and (c) show 45℃ tilt angle SEM images of the samples prepared at substrate temperatures of 500℃, 600℃, and 800℃, respectively. They were thoroughly nanostructured, and many features of a size in the 100 nm range were observed. Figure 2 (b) exhibits sharp asperities with a high field enhancement factor. The field emission current densities (not shown) at substrate temperatures up to about 500℃ are nearly constant at the threshold field but rapidly improve at substrate temperatures over 600℃. The better field emission at a substrate temperature of 600℃ most likely resulted from the high field enhancement factor.

Figure 3 shows changes in Raman spectra for the a-C films as a function of substrate temperature. All spectra had two peaks at about 1365 cm^{-1} (D) and about 1580 cm^{-1} (G), which characterized the presence of a disordered sp^2 phase and well-crystallized graphite, respectively [14]. The two peaks indicate typical spectra of a-C films. Similar results were observed by Dillon et al. [15] for carbon films post-annealed up to 950℃ after growth by an ion beam sputtering system. At the substrate temperature of 600℃, the D peak started to become sharper and stronger, and a new band appeared at about 1625 cm^{-1}. These spectra were analyzed by Gaussian fitting to the data as a sum of the D and G peaks. The variation of the width [full width at half maximum (FWHM)]of the D and G peaks as a function of substrate temperatures are shown in Figure 4 (a). The overall trend is a decrease in the G and D line widths as substrate temperature increases, with the most rapid decrease occurring at about 600℃.

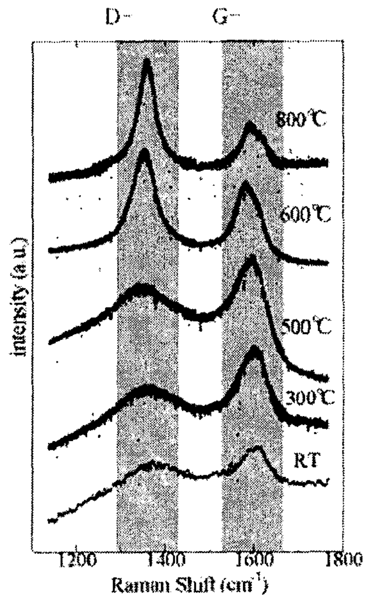

Fig. 3 Raman spectra for the a-C films for a series of substrate temperatures

Figure 4 (b) shows the I(D) / I(G) intensity ratio as a function of substrate temperature. The behavior of the intensity ratios at substrate temperatures from RT up to about 500℃ was nearly constant, but this rapidly increased at a substrate temperature of 600℃.

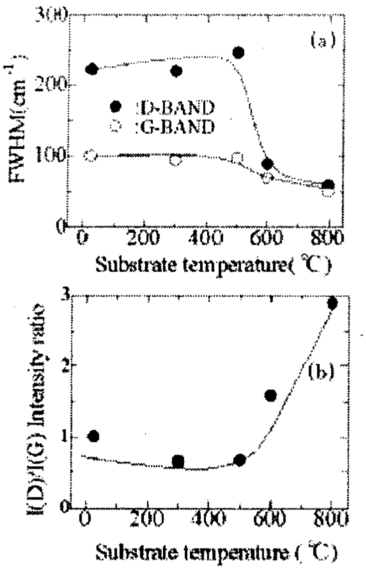

Fig. 4 (a) FWHM of D and G peak as a function of substrate temperature, (b) I(D) / I(G) intensity ratio as a function of substrate temperature

This behavior can be explained as follows. At substrate temperatures higher than 500℃, the graphite crystallites grow in size and number, and this causes the widths of the D and G peaks to decrease and the I(D) / I(G) ratio to increase [15].

4. Summary

a-C films have been prepared by using RF plasma enhanced CVD in pure methane plasma as a function of substrate temperature. The surface morphology and graphite crystallite size of the a-C thin films were significantly changed with increasing substrate temperature. In particular, at a substrate temperature higher than 500℃, the graphite crystallites grow in size and number, and that causes the widths of the D and G peaks to decrease and the I(D) / I(G) ratio to increase.

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