Deposition of a-C:H/diamond thin film on the heated Fe/Si substrate in CH4 rf discharge

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The hydrogenated hard carbon films were deposited at elevated temperature in a planar rf CH_4 plasma. The deposition rate, and mechanical and optical properties of the carbon films deposited at substrate temperature between room temperature and 400℃, were examined. The activation energies of around 0.04 - 0.05 eV at gas pressures of 40 - 100 mTorr were obtained from the Arrhenius plots of the deposition rates on Si substrate. The value of the activation energy suggest that ionic species play an important role in the incorporation of the physisorbed CH_3 radicals. The dense carbon films having film densities up to 2.7 g/cm^3 were obtained at 40 mTorr. The hydrogenated carbon films deposited on Fe/Si substrate contains an etching-proof layer which is very thin, and is formed at the interface between hydrogenated carbon layer and Si substrate. Using a hot plasma chemical vapor deposition, diamond film was deposited on the etching-proof layer. The nucleation density of the diamond on the etching-proof layer was higher than that on the Si wafer.

1. INTRODUCTION

Amorphous hydrogenated carbon (a-C:H) films have numerous useful properties such as transparency for ultraviolet, visible, and infrared light, low refraction index for infrared light, high mechanical hardness, high electrical resistivity and chemical inertness, and a low friction coefficient. Therefore, they can be applied as anti-reflection and scratch protective coatings on infrared optics, and also for wear resistance for industrial purpose. Although many researchers have been reported the deposition of these carbon films, several questions on the deposition process still remain[1].

The present paper describes the deposition rate and the properties of the carbon films deposited on the elevated substrate temperature in a CH_4 rf plasma. From these results, we discuss the growth mechanism of the a-C:H film and the effect of substrate temperature on film properties.

2. EXPERIMENT

The a-C:H films were deposited in a cylindrical plasma chamber with a parallel plate electrode configuration. A scheme of an experiment equipment for the film deposition is illustrated in Fig.1. The parallel cathode (powered) and anode (grounded) electrodes consist of stainless-steel disks 153 mm in diameter with a spacing of 50 mm. A power supply used to generate the plasma is a 13.56 MHz rf oscillator, and a power input was always kept at 70 w. A CH_4 gas as a source material was introduced into the reaction chamber, and a gas pressure during the deposition was measured by a capacitance manometer. A temperature of Si substrate placed on the cathode electrode was varied by heating with a resistance heater, which is located inside the cathode electrode disk.

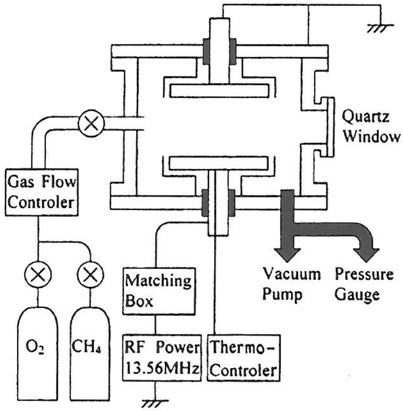


Fig.1 A schematic diagram of a rf plasma chamber.

The substrates used were monocrystalline Si wafer and Fe/Si wafer of which thin Fe film was evaporated on a Si wafer surface. The deposition rate was determined with the film thickness and the deposition time. The X-ray diffraction (XD) and X-ray photoelectron microscope (XPS) measurements were carried out to characterize the deposited films.

3. RESULTS AND DISCUSSIONS

3.1 Mechanistic study on the deposition process

The deposition rate of a-C:H film on Si substrate was measured as a function of CH_4 gas pressure and a substrate temperature, as shown in Fig.2. It indicates remarkable decrease especially until to 200℃, and then decreased monotonically with the increase of substrate temperature, at each pressure. In this work a power supply to the substrate heater was turned off during the film deposition, because the thermo-controller was strongly perturbed by the rf signal. Therefore, the substrate temperature decreased from an initial temperature during the deposition process, and the substrate shifted from 400℃, 300℃, 200℃ and 100℃ until to 250℃, 200℃, 150℃ and 80℃, respectively, after the deposition for 30 min. The substrate temperature indicated in Fig.2 means the initial temperature. Nevertheless, the deposition rate provided at each initial temperature will be fluctuated (increased) by only a small value from a deposition rate which would be expected for constant substrate temperature. Because, the change in the deposition rate at temperatures more than 200℃ becomes relatively low, as a shown in Fig.2. However, the film properties towards the depth in the film will be somewhat changed, especially in the hydrogen content and the hydrogen network.

Figure 3 shows the Arrhenius plots of the deposition rates given in Fig.2. The calculated activation energy is around 0.04 - 0.05 eV for each gas pressure condition. It is well known that the precursor for the deposition of a-C:H film in CH_4 plasma will be CH_3 radicals[1]. The residence time on the substrate surface of CH_3 is described by Frenkel equation, $\tau = \tau_0 \exp (E_{des} / k T)$, where τ_0 is the minimum residence time, E_{des} is the desorption energy, and T is the substrate temperature[2,4]. The desorption energy of CH_3 radical have been reported as $E_{des} \sim 0.65$ eV[2-4]. But the activation energy obtained in this work is much less than 0.65 eV. If the a-C:H film in CH_4 plasma grows through only spontaneous incorporation of physisorbed CH_3 radical, it would be 0.65 eV. However the activation energy obtained in this work is much less than 0.65eV. This difference suggests that ionic species play an important role in the incorporation of the physisorbed CH_3 radicals. The incorporation of ions in the growing film does not play a major role, because if it is predominant process, the film deposition rate does not depend on the substrate temperature.

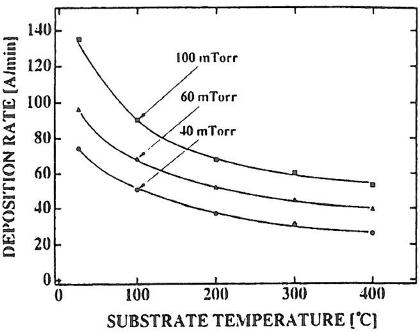


Fig.2 The deposition rates of a-C:H films deposited at pressure of 40, 60 and 100 mTorr, and at substrate temperatures between room temperature and 400℃.

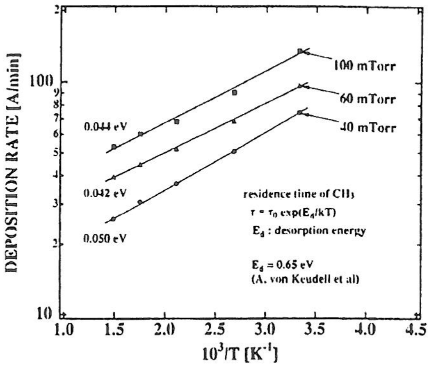


Fig.3 The Arrhenius plots of the deposition rates of a-C:H films. The deposition rates shown in Fig.2

3.2 Properties of a-C:H films on Si substrate

Figure 4 shows the film density of carbon films on the Si substrate, as a function of substrate temperature. The density of carbon films increases with the increase of substrate temperature at 40 mTorr, especially more than 300℃, and reaches to 2.7 g/cm^3 at 400℃. At other gas pressures, the film density indicated only a small increase with increasing substrate temperature, and indicated around 2.0 g/cm^3 which is a typical value of DLC film[1]. The density of this dense carbon film (2.7 g/cm^3) is larger than that of graphite (2.26 g/cm^3), and is lower than that of diamond (3.51 g/cm^3) and SiC (2.7 g/cm^3). Figure 5 shows the substrate temperature dependence on the hardness of carbon film. It also increases with the increase of substrate temperature, especially more than 300℃. In order to evaluate the components of dense carbon film, XD and XPS measurements were carried out. The XD analysis of the dense carbon film indicates no any other diffraction peaks than that of Si, suggesting that the film mainly consists of an amorphous carbon phase. The XPS spectra of C(1s) and Si(2p) signals are measured for different Ar^+ sputtering times from the carbon film surface. The XPS signal indicated that the film consists of predominant disordered carbon, and very thin SiC layer at Si substrate surface. Hence, the high film density will not be due to the formation of SiC, and is rather due to the formation of disordered sp^3-type carbon. The IR absorption spectra of the films were also measured. A small amount of sp^2-type carbon are also obtained in the films deposited at substrate temperatures more than 300℃, which may be due to the recombination of dangling bonds created by the increase of the substrate temperature.

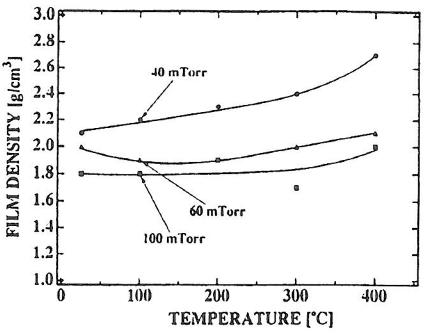


Fig.4 The densities of a-C:H films deposited at pressure of 40, 60 and 100 mTorr, and at substrate temperatures between room temperature and 400℃.

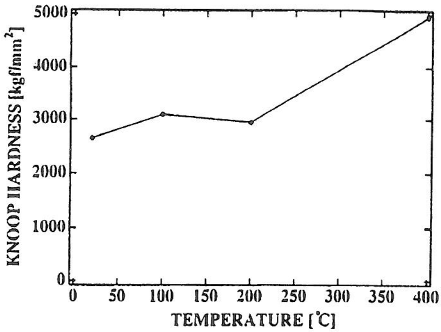
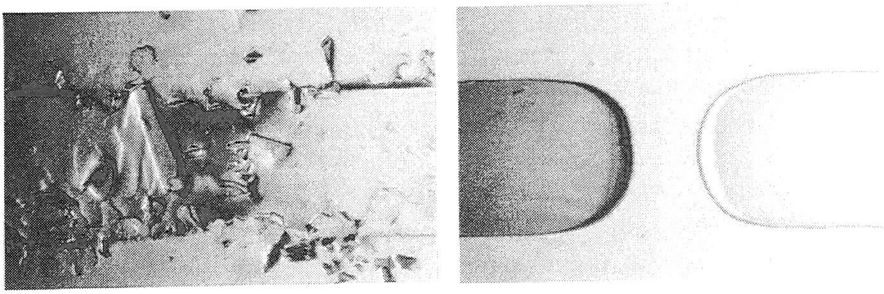


Fig.5 The Knoop hardness of a-C:H film deposited at 40 mTorr as a function of substrate temperature.

3.3 Properties of a-C:H films on Fe/Si substrate

The a-C:H films were deposited on Fe/Si substrate, and the Fe thin film was partially evaporated on the Si substrate surface with a patterned mask. After the film deposition, the samples were etched in a CF_4 rf plasma for 30 min. During the etching process, the a-C:H layer containing Fe_xC_y phase formed on the substrate surface was completely etched away. SEM photographs of the samples prepared at 60 mTorr and temperatures of room temperature and 400℃, after the etching process are shown in Fig.6. A semi-dark (patterned) region of the sample at 400℃ corresponds to an area of the Fe thin film evaporated. At this region an etching-proof layer which is very thin, is generated at the interface between a-C:H layer and Si substrate, and acts as an etching mask. Accordingly, Si substrate at this region remains, and other part of Si is etched. At room temperature, the etching-proof layer was scarcely formed, so that a clear mask pattern was not obtained, as shown in Fig.6. Although the characterization of the etching-proof layer is somewhat difficult because of very thin thickness, it will contain predominantly the diamond phase. The diamond growth was carried out by the hot-plasma CVD method using a bare Si wafer and the substrate prepared at 400℃ indicated in Fig.6. The nucleation density of the diamond on the etching-proof layer was higher than that on the Si wafer.



(a) room temperature (b) 400℃

Fig.6 The photogragh of the surface prepared at 60 mTorr and temperatures of room temperature and 400℃, after the etching process.

4. CONCLUSION

The deposition rate and the properties of a-C:H films depending on substrate temperature were examined in a CH_4 rf plasma. The temperature dependence of the film deposition rate suggests that the ions play an important role in incorporation of physisorbed CH_3 radicals. The dense carbon films having densities more than that of the DLC film can be formed at pressure condition of 40 mTorr. The a-C:H films deposited on Fe/Si substrate included the etching-proof layer. The synthesis of diamond on an etching-proof layer in hot plasma CVD was carried out. The nucleation density of the diamond on the etching-proof layer was higher than that on the Si wafer.

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