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FABRICATION OF C60-BASED THIN FILMS BY LASER ABLATION AND ION PLATING METHODS

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C60-based thin films were prepared by two methods, i.e. KrF-excimer laser ablation and rf-plasma ion plating. Laser deposition films prepared at energy fluences between 40mJ/cm^2 and 50mJ/cm^2 were confirmed to have a single phase of C60 from their Raman, and UV-VIS absorption spectra and HPLC analysis. These films had surfaces with rms roughness of less than 1nm, far smoother than the surfaces of films deposited by conventional vacuum evaporation. The structure of films deposited by an ion plating method varied from C60-dominant phase to amorphous carbon-dominant phase with an increase of applied rf-power from 1W to 10W. The ion plating films had higher adhesion strength to the substrate than the films prepared by the laser ablation and conventional vacuum evaporation.

1. Introduction

Since the development of the contact-arc method for highly efficient production of fullerene[1], physical properties of fullerenes have been extensively investigated with a focus on the superconductivity of doped C60 solids.[2] The applications of C60 to mechanics and electronics are also expected from its novel nano-ball molecular structure and semiconducting property in the solid state, respectively. Rectifying effects of C60 were recently reported for the heterojunctions composed of Al/AlOx/C60[3]. A nano-scale ball bearing is considered to be one of novel applications utilizing the unique structural features of C60 molecule. Regueio et al. reported using a simple elasticity argument that C60 molecule is stiffer than diamond.[4]

C60 thin films provide specimens useful not only for measuring physical properties but also for applying to electronic devices and solid lubricants. Fullerene thin films have been fabricated mostly by vacuum evaporation and in some cases by MBE[5]. Few attempts have been made to prepare fullerene films by other methods and to modify the film structure. In this study, we have examined the optical and mechanical properties of C60-based films fabricated by novel processes. For the film fabrication, we employed pulsed laser deposition and rf plasma assisted ion plating. The structure and properties of the films prepared by these new methods are investigated in comparis on with those of films prepared by the conventional vacuum evaporation.

2. Experimental

2-1. Preparation of C60-based films by pulsed laser deposition

The film deposition chamber used is schematically illustrated in Fig.1. A pulsed KrF excimer laser beam (duration time 23ns, 1-10Hz frequency) was focused on a 2mm x 6mm spot of a C60 target which was made by pressing purified C60 powders (purity > 99.5% measured by HPLC analysis).

The laser energy fluence at the target was changed in the range between 20mJ/cm^2 and 250mJ/cm^2. Films were deposited on Si(111) or fused silica substrates placed 3cm away from the target at room temperature (about 25°C) and under the atmosphere of 3x10^{-3} Torr He.

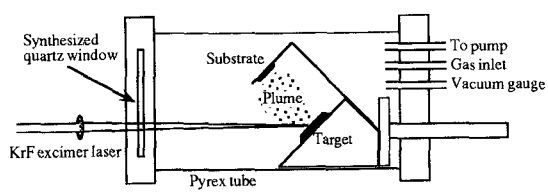

Fig.1. Schematical illustration of pulsed laser deposition chamber.

2-2. Preparation of C60-based films by ion plating and vacuum evaporation methods

Figure 2 shows the schematic diagram of ion plating apparatus which is composed of a typical vacuum evaporator. An rf power (13.56MHz) was applied to a 2.5 turn stainless coil of 15cm in diameter to generate the rf plasma in 1x10^{-3} Torr Ar atmosphere. The minimum rf power to generate Ar plasma was 1W. C60 powder was evaporated from an alumina crucible heated at 500°C, passed through the Ar plasma and deposited into film on a substrate.

Prior to the evaporation, C60 powder was pre-heated at 270°C for 2h under 10^{-5} Torr for removing adsorbed solvents. Films were deposited at room temperature or 150°C under $1x10^{-3}$ Torr Ar on Si(111) or fused silica substrates as well as on steel rods (2mm in diameter and 30mm in length) for the measurement of frictional property.

Vacuum evaporation C60 films were also prepared using the ion plating chamber without applying rf power.

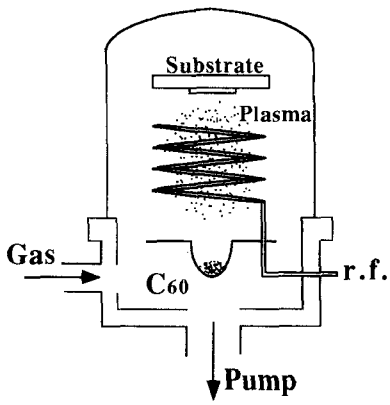

Fig.2. Schematical diagram of ion plating apparatus.

2-3. Film characterization

The deposited films were characterized by means of Raman spectroscopy and UV-visible (VIS) absorption spectroscopy. The atomic-scale surface morphology was examined by an atomic force microscope (AFM) (Nanoscope II). Mechanical and tribological properties of the films were investigated using a scratch tester, an ultramicrohardness tester and a pendulum type friction tester .

3. Results and Discussion

3-1. Film deposition

The film deposition rate in the pulsed laser (1Hz frequency) deposition increased from 0.05nm/min to 3.0nm/min with an increase of laser energy fluence from 30mJ/cm^2 to 40mJ/cm^2. The deposition rate at a laser energy fluence of 250mJ/cm^2 was 7.0nm/min. The red plume emission during the ablation at 40mJ/cm^2 and higher may correspond to the photoluminescence peak at about 750nm.[6]

Deposition rates in the ion plating with rf powers between 1W and 10W were constant 0.7nm/min, which was higher by 40% than that in the vacuum evaporation (0.5nm/min). The vacuum evaporation film deposited at room temperature showed no clear XRD peaks, but the films deposited on Si(111) at 150°C showed XRD peaks assigned to C60-fcc structure.

3-2. Optical properties of the C60-based films

Figure 3 shows UV-VIS absorption spectra of a vacuum evaporation C60 film, pulsed laser deposition films at laser energy fluences of 40mJ/cm^2 and 120mJ/cm^2, and ion plating films at rf powers of 1W and 5W. All the films were deposited on fused silica substrates at room temperature. The spectra of 40mJ/cm^2 laser deposition and vacuum evaporation films were identical to each other. The absorption maxima at 220nm, 268nm, 346nm and 442nm are assignable to the interband transitions among π orbitals in C60 films[7]. The absorption peaks characteristic to C60 were not visible for the films of laser deposition at 250mJ/cm^2 and of ion plating at 5W rf power. Apparently, C60 content in these films decreased and photo or plasma chemically decomposed carbon components increased. The presence of C60 was clearly indicated in the ion plating film made at 1W rf power by the broad absorption maxima described above.

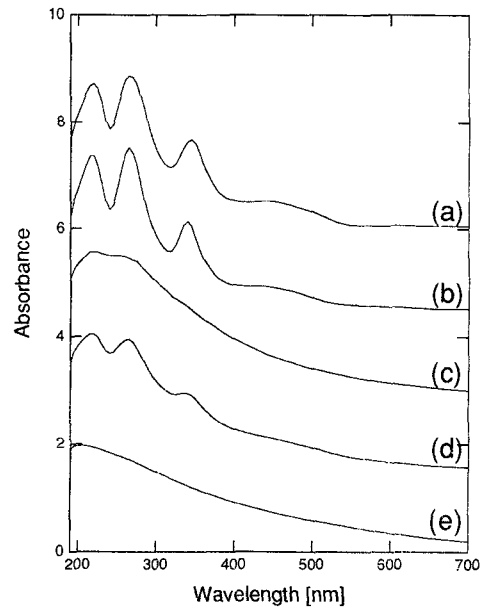

Fig.3. UV-VIS absorption spectra for the vacuum evaporation C60 film (a), laser deposition films at 40mJ/cm^2 (b) and 250mJ/cm^2 (c), and ion plating films under rf=1W (d) and 5W (e).

Figure 4 shows the Raman spectra of films deposited by various methods on Si(111) substrates at room temperature. The spectra of vacuum

evaporation and 40mJ/cm^2 laser deposition films were essentially the same as those of previously reported C60 film[8] and Si. These films dissolved in benzene without any residues. The resulting solution showed no HPLC peak other than C60 peak. The film deposited at a laser energy fluence of 120mJ/cm^2 did not exhibit Raman peaks characteristic to C60 film. The ion plating film at 1W rf power showed weak peaks corresponding to C60, but the peaks become invisible in the films deposited at higher rf powers. Both the 250mJ/cm^2 laser deposition film and the 5W rf ion plating film had broad Raman peaks assignable to amorphous carbon around 1600cm^{-1} and 1350cm^{-1}.

Thus, by controlling either the laser energy fluences applied to the target ablation or rf power to generate the plasma, we could modify continuously the structures and properties of deposited films between those of pure C60 and photodecomposed species, such as amorphous carbon.

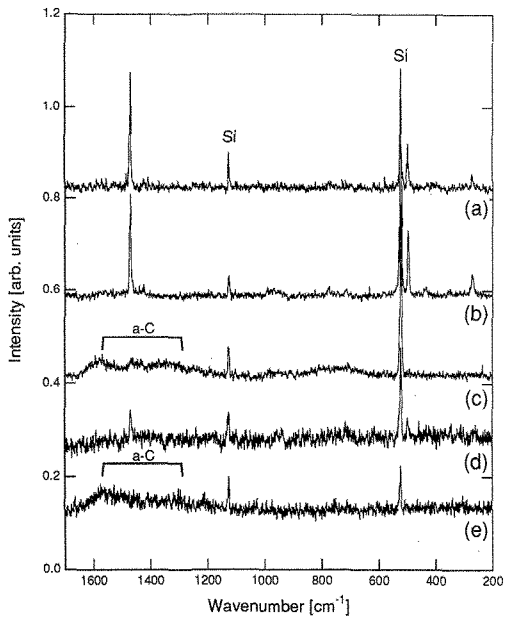

Fig.4. Raman spectra of the vacuum evaporation C60 film (a), laser deposition films at laser energy fluences at 40mJ/cm^2 (b) and 250mJ/cm^2 (c), and ion plating films under rf=1W (d) and 5W (e).

3-3. Surface morphology of the C60-based films

Figure 5 shows AFM images of 2μm x 2μm surfaces for the vacuum evaporation film (a) and the 40mJ/cm^2 laser deposition film (b), both deposited on Si(111) substrates at room temperature. These AFM images clearly demonstrate that the surface of laser deposition C60 film (b) is much smoother than that of the vacuum evaporation C60 film (a); the root-mean-square (rms) roughnesses were evaluated to be 5.08nm and 0.38nm for the vacuum evaporation and laser deposition films, respectively. It is noteworthy that the rms roughness of the laser deposition C60 thin film is less than the diameter of C60 molecule (about 0.7nm). This extremely smooth surface of the laser deposition C60 film is considered to originate from the enhanced surface migration of C60 molecules arriving with high kinetic energy supplied from photoexcited ablation process. The rf=1W ion plating film had a rms roughness of 3.75nm, which was also smoother than that of the vacuum evaporation film. The surface roughness of the ion plating films increased with an increase of rf power applied.

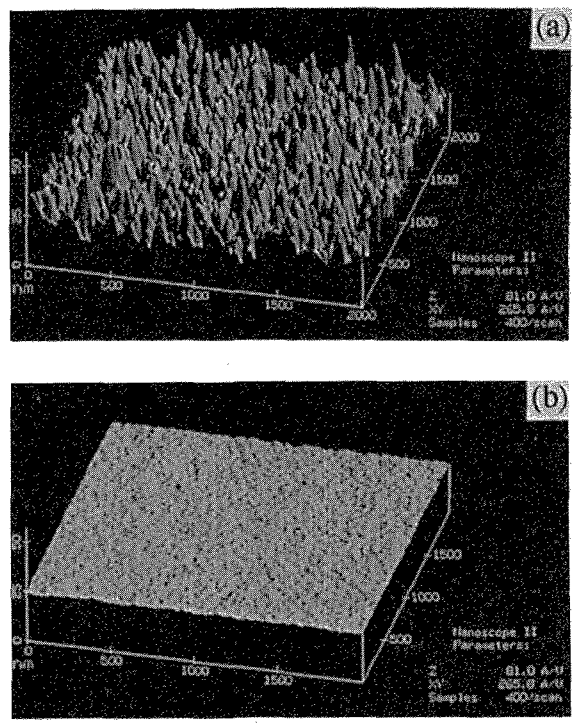

Fig.5. AFM surface images of vacuum evaporation C60 film (a) and 40mJ/cm^2 laser deposition C60 film (b). (image size: 2μm x 2μm).

3-4. Mechanical properties of the C60-based films

Figure 6 shows the adhesion strength of the laser deposition (a) and the ion plating (b) films to Si(111) substrate. Here, the adhesion was estimated from the load applied to a needle when the film was torn from the substrate. The adhesion force of the

rf=1W ion plating film was 12mN, higher than that of the vacuum evaporation film, 5mN. The load for film scratch in the ion plating films increased lineally with the increase of rf power. The load of the laser deposition films also increased lineally with an inclination of adhesion force rate as half as that of the ion plating film.

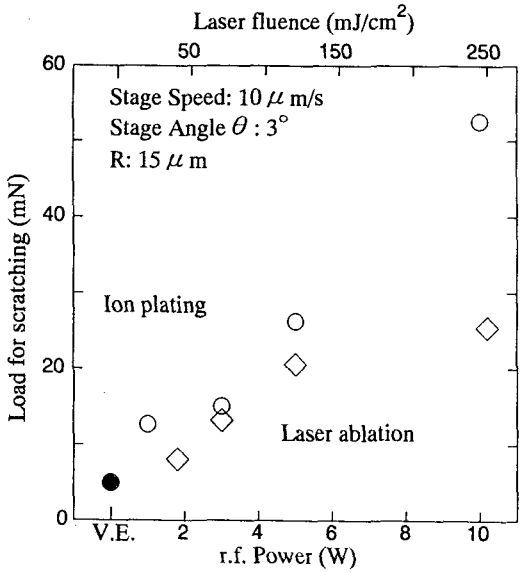

Fig.6. Results on scratching test adhesion between Si(111) substrate, and vacuum evaporation (●), laser deposition (◇) and ion plating films (○). The adhesion was estimated from a load applied to a needle when the film was torn from the substrate.

In order to examine the possibility of C60 film as a lubricant, friction coefficients were measured for the vacuum evaporation and the ion plating films deposited on steel rods at 150°C. Initial friction coefficients (f_i) of all the films were 45% lower than that of a bare steel rod (f_i(films)=0.25, f_i(bare steel rod)=0.45). Recently Bhushan et al. reported the friction coefficient of 0.2 for vacuum evaporation C60 films, close to the present value[9]. Such a low friction was maintained far much longer time by the coating with ion plating film than by the coating with vacuum evaporation film. Further studies are now in progress in order to examine the effect of preparation conditions on the tribological performance of films.

4. Conclusions

Pulsed KrF excimer laser ablation using a C60 target was applied to prepare C60 thin films. The C60 films deposited at laser energy fluences between 40mJ/cm^2 and 50mJ/cm^2 showed atomically smooth surfaces. Rf-plasma excited ion plating films contained decomposed carbon matrix and exhibited a strong adhesion between substrate and film. Friction coefficients of C60-based films were estimated to be 0.25, about a half of steel rod. Laser ablation and ion plating methods can be used for fabricating multi-layered C60-containing films with continuously modified structures by applying variable photo- or plasma excitation.

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