Deposition of Ti-Containing Diamond-Like Carbon Films on Interior Surface of Tubes by Plasma Source Ion Implantation

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A plasma source ion implantation (PSII) method for the deposition of metal-containing diamond-like carbon (DLC) films on the interior surface of tubes was developed. A magnetron sputter source equipped with a Ti target was used as a plasma source and a metal source. Argon/acetylene-mixed gas was used as the working gas for plasma. A negative high-voltage pulse (~10 kV, 100 Hz, 100 µs) superposed on a DC voltage of ~0.5 kV was applied to the substrate tube. The chemical composition and microstructure of these films were characterized by Auger electron spectroscopy, X-ray photoelectron spectroscopy, X-ray diffractometry, high-resolution transmission electron microscopy and micro-Raman spectroscopy. Uniformity in the thickness of deposited DLC films was confirmed and the structures of Ti-containing DLC films were examined.

1. Introduction

Metal-containing diamond-like carbon (metal-DLC) films with properties intermediate between DLC and metal carbide have been shown to have a small friction coefficient, a low abrasive wear rate and good adhesion to metal substrates.(1,2) Metal-DLC films have been used for the investigation of nanocomposite films with microstructures consisting of nanocrystalline grains in an amorphous matrix.(3) Several techniques have been proposed for the deposition of metal-DLC films, which include sputter deposition,(4–6) plasma-assisted chemical vapor deposition (CVD),(7) ion-beam-assisted deposition (IBAD),(8) and magnetron plasma source ion implantation (PSII).(9–11) Recently, plasma source ion implantation for the interior surface of tubes has been developed.(12)

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In this paper, we developed a PSII method for metal-DLC film deposition for the interior surface of cylindrical bores based on RF plasma decomposition and reactive sputtering. A magnetron sputter source was used as a plasma source and a metal source for the PSII method. Titanium-containing DLC films were deposited by the PSII method in an argon/acetylene mixture from a Ti sputter target. The DLC films were characterized by Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), glancing-angle X-ray diffractometry (GXRD), high-resolution transmittance electron microscopy (HREM) and micro-Raman spectroscopy.

2. Experimental

2.1 PSII apparatus

A PSII apparatus for ion implantation and DLC film deposition of the interior surface of a tube has been developed. Figure 1 shows schematically the experimental equipment. A type-304 stainless-steel tube 120 mm in inner diameter and 200 mm in length was used as a substrate tube for PSII. A silicon wafer strip 10 mm wide and 200 mm long was set in the tube for the analysis. A Ti disc 2 inches in diameter was used as the sputtering target. A magnetron sputter source was inserted into the tube. The plasma was generated by the application of a 13.56 MHz, 150 W RF power to the magnetron sputter source. The PSII method developed in this study was used for metal ion implantation. At first, Ti ion implantation was preformed to estimate the capability of metal ion implantation into the interior of a tube by this method. Ti was used as a sputter target with argon gas. A pulse voltage of –16 kV was applied to the substrate tube at a pulse repetition rate of 1 kHz and a pulse duration of 10 μs. For the preparation of metal-DLC films, argon and acetylene gases were introduced into the discharge chamber at a constant rate. The film composition was
changed by changing the flow rates of argon and acetylene gases. A pulse voltage of –10 kV superposed to a DC voltage of –0.5 kV was applied to the substrate tube at a pulse repetition rate of 100 Hz and pulse duration of 100 μs.

The magnetron sputter source was moved stepwise along the axis of the substrate tube to obtain uniform ion implantation and DLC film deposition during the experiments. The chemical composition and chemical state of the films were evaluated by AES and XPS under Mg Kα X-ray irradiation. Film thickness was monitored by cross-sectional scanning electron microscopy (SEM) observation. The structural information was studied by GXRD with an incident angle of 0.5 degrees and by HREM. The chemical structure of the DLC films was evaluated by micro-Raman spectroscopy.

A ball-on-disc type of apparatus was used for the tribological test. Balls of tungsten carbide WC, 6 mm in diameter, were used. Friction coefficients were estimated using a ball-on-disc arrangement with a normal load of 2 N, and a velocity of 100 mm/s.

3. Results and Discussion

The surface layers of Ti-implanted silicon wafers were examined by AES. Figures 2(a) and 2(b) show AES depth profiles of Ti-sputter-deposited samples with no pulse and Ti-implanted samples with pulse conditions of –16 kV, 1 kHz, and 10 μs, respectively. It is apparent from Fig. 2(b) that Ti atoms penetrated into the substrate and a mixed zone at the interface was formed.

The thickness distribution of the DLC films prepared on Si wafers placed on the inside of the tube was examined using pure acetylene gas. Figure 3 shows the thickness of DLC films on the Si wafers as estimated by cross-section SEM observation. The distance 0 mm on the x-axis is the top end of the tube. Although the thickness at the distance 0 was greater than that at other locations, there was no big difference from that at the other locations.

The surface morphology of Ti-containing films observed by SEM was very fine and granular for film coatings containing 0–9 at.% Ti, and the grain size increased with metal content.

![Fig. 2. Auger depth profiles of sputter-deposited Ti film without pulse (a) and with pulse (b).](image)
Raman spectroscopy is a very useful method of evaluating the chemical structure of carbon films. Figure 4 shows the Raman spectrum of the 9-at.%-Ti-containing DLC film. A broad peak typical of DLC films was observed at a range between 1000 cm$^{-1}$ and 1700 cm$^{-1}$ for all films. The spectral profile was fitted by two Gaussian profiles centered at 1404 cm$^{-1}$ corresponding to the D-line assigned to a disordered structure, and at 1579 cm$^{-1}$ corresponding to the G-line assigned to the graphite structure. The integrated intensity ratio ($I_D/I_G$) has been correlated with the sp$^2$/sp$^3$ bonding ratio.$^{(13)}$ The $I_D/I_G$ ratio of 2.84 was derived from Fig. 4. This value is larger than the common value for DLC films.$^{(14)}$

Figures 5(a) and 5(b) show C1s and Ti2p XPS spectra of 21-at.%-Ti-containing DLC film. For the C1s spectrum, the main peak at 284.2 eV was assigned to amorphous carbon and the photoelectron, which was assigned to TiC bonding (281.6 eV$^{(15)}$), was observed as a shoulder at the lower binding energy (BE) side. On the other hand, for the Ti2p spectrum, a single peak at 454.8 eV, which was assigned to TiC bonding (454.6 eV$^{(15)}$), was observed.

Figure 6 shows GXRD patterns for Ti-containing DLC films. The crystalline TiC phase was formed at Ti contents of 19 and 21 at.%. The results of X-ray examination were confirmed by HREM. Figure 7 shows a HREM image and a selected-area electron diffraction pattern of 19-at.%-Ti-containing film. Diffraction rings consisting of small dots were observed. These rings were assigned to the TiC crystalline phase. The nanoscale TiC crystals, whose diameter was around 5 nm, were clearly observed.

Ball-on-disc tests were performed to estimate the tribological property of metal-DLC films. The friction coefficient of the metal-free DLC film was around 0.1 after 10000 rotations. SEM observation of this film after the wear test showed only a very fine wear track and no sign of peeling off was observed on the wear track. The friction coefficient increased with Ti content for the Ti concentration range prepared in this study.
4. Conclusion

A PSII apparatus for the implantation and coating of DLC films on the interior surface of a tube was developed. Metal ion implantation into the interior surface of a tube was performed by the PSII method. Ti-containing DLC films were prepared using the PSII apparatus. The capability of uniform DLC and metal-DLC film deposition on the interior surface of a tube was confirmed. The structure of the films changed from metal-containing amorphous to crystalline carbides with increasing metal content.
Fig. 6 (left). X-ray diffraction patterns of Ti-containing DLC films.
Fig. 7 (right). High-resolution transmittance electron microscopy image and selected-area electron diffraction pattern of 19-at.%-Ti-containing DLC film.

References