

Electrical and Mechanical Characteristics of Precious Metal-Doped Carbon Films

I. Uesaka¹⁾, Y. Mochizuki¹⁾, S. Matsuhashi¹⁾, S. Umemura¹⁾,
S. Hirono²⁾, and R. Kaneko³⁾

¹⁾ Chiba Institute of Technology, Tsudanuma 2-17-1, Narashino-shi, Chiba 275-0016 Japan,
e-mail: g0279003@cc.it-chiba.ac.jp

²⁾ NTT AFTY Corporation, Shimorenjaku 4-16-3, Mitaka-shi, Tokyo 180-0013 Japan

³⁾ Faculty of Systems Engineering, Wakayama University, Sakaedani 930, Wakayama-shi,
Wakayama 640-5810 Japan

We deposited Au-, Pd- and Pt-doped carbon films onto silicon substrates to clarify the mechanical and electrical properties of various metal-doped carbon films. We did this analysis using RF sputtering and we also evaluated the morphology, resistivity, wear durability, and carbon sp³ and sp² fraction of the films. The resistivity of the Pt-doped carbon film decreased with an increase of the Pd concentration. However, the resistivity of the Au- and Pd-doped carbon films showed no significant change with an increase of the dopant concentration. The durability of the Pt-doped carbon film also degraded with an increase in the dopant concentration, and the wear durability of the Au- and Pd-doped carbon films showed no degradation with an increase in the dopant concentration. The resistivity and wear durability characteristics of the films are discussed in conjunction with the carbon sp³ and sp² fractions in the films.

Key word: metal-doped thin films, RF sputtering, resistivity, wear durability

1. INTRODUCTION

Amorphous, carbon-thin films are used in various fields as coating applications. For instance, hydrogenated carbon films are used as protective films for magnetic heads and media in hard disk drives [1]. In general, highly wear durable amorphous carbon films, such as a-C:H and ta-C, are electrically nonconductive. If a highly wear durable and conductive film was developed, it would have various applications. Metal doping of carbon is one way to produce conductive and wear durable films. The use of metal-doped hydrogenated carbon films as tool coatings and to improve adhesion has been

investigated [2]. However, we surmise that the metal doping of non-hydrogenated carbon films will be more effective in achieving conductive and wear durable films. Previous research shows that Ir doping of non-hydrogenated carbon is the most effective way to achieve wear durable and conductive carbon films [3]. Furthermore, research shows that the metal doping of non-hydrogenated carbon films has non-tribological applications, such as use in a nanogranular magnetic recording medium by Co-doped carbon [4] and as an electrochemical sensor electrodes using Ni-doped carbon [5]. Hence we deposited carbon films doped with various types of metal and investigated their

electrical and mechanical characteristics. In this paper, we discuss the electrical and mechanical characteristics of Au-, Pd- and Pt-doped carbon films.

2. EXPERIMENT

We used RF sputtering to deposit metal-doped and non-doped carbon films onto silicon substrates. The dopant metals were Au, Pd, and Pt. Each metal pellet was the same size so as to keep the sputtering conditions constant. Each pellet was placed on a carbon target for doping. All films were deposited at a thickness of about 40 nm. The substrate temperature was kept at 200 °C during the deposition. We estimated the metal concentrations in doped carbon films from the ratio of the area of the metal pellets to the carbon target, and from the ratios of the sputtering rates of carbon to each metal [6]. The metal concentration was given by

$$S_M R_M / \{ (S_C - S_M) R_C + S_M R_M \},$$

where R_C and R_M are the respective sputtering rates [atoms/ion] of carbon and metal, and S_C and S_M are the areas, in [mm²], of carbon and metal.

The surface roughness of the films was measured by AFM. The resistivity of the deposited films was evaluated by the four-terminal resistance measurement method [7]. The sheet resistance of each film was measured by this method and the resistivity was estimated from the product of the sheet resistance and the film thickness. The wear durability of the films was evaluated by AFM nanowear tests [8, 9]. In the tests, the scan size was $1 \times 1 \mu\text{m}$ and the applied load was 40 μN . The wear depth was obtained from cross-sectional images of wear marks. A three-sided pyramidal diamond stylus was used throughout the evaluations. Furthermore, carbon sp³ and sp² fractions of the films were estimated by the deconvolution of the XPS carbon 1s spectra.

3. RESULTS AND DISCUSSION

3.1 Surface roughness of the films

Figure 1 shows the relationship between the arithmetic mean roughness (Ra) and the dopant concentration of Au-, Pd-, and Pt-doped carbon films. Here, Au-, Pd-, and Pt-doped carbon films are abbreviated as Au-C, Pd-C, and Pt-C. The surfaces of the doped carbon and non-doped carbon films were very smooth and there was little change in the Ra regardless of the dopant concentration for three doped films. If the dopant metals aggregate in the as-deposited films, the surface roughness should be much larger than the roughness values shown in Fig. 1. Hence, it is surmised that aggregation of dopant metals did not occur during the deposition and that the dopant metals have been uniformly distributed in the films.

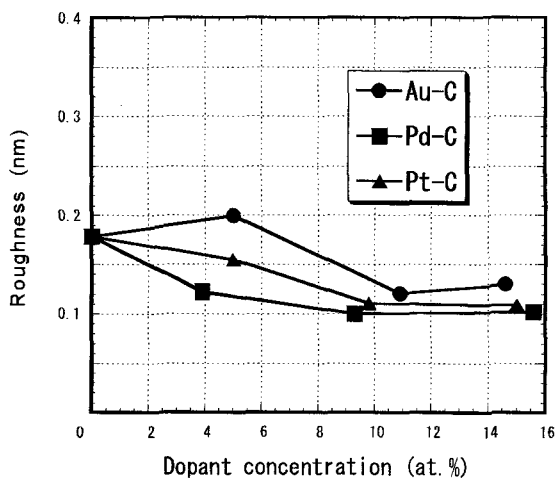


Fig. 1 Relationship between resistivity and dopant concentration of Au-, Pd-, and Pt-doped carbon films

3.2 Resistivity of the films

Figure 2 shows the relationship between the resistivity and the dopant concentration of Au-, Pd-, and Pt-doped carbon films. The resistivity of Pt-C decreased with an increase in the dopant concentration.

However, the resistivity of Au-C showed little change with an increase of the Au concentration to 10.9 at.%, and it decreased at 14.6 at.%. The resistivity of Pd-C also showed little change when the Pd concentration was increased to a concentration of 9.3 at.%, and it increased at 15.6 at.%. The resistivity characteristics of three doped films are discussed in conjunction with carbon 1s spectra analysis by XPS in section 3.4.

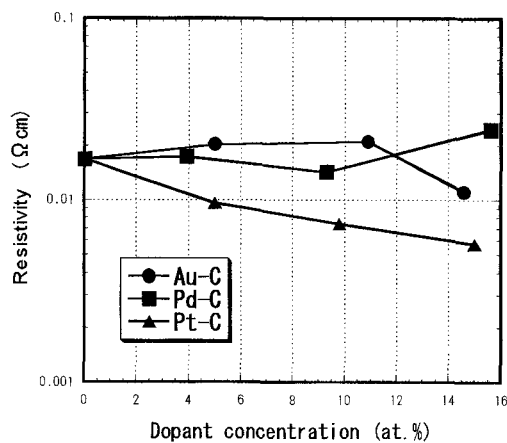


Fig. 2 Relationship between resistivity and dopant concentration of Au-, Pd-, and Pt-doped carbon films

3.3 Wear durability of the films

Figure 3 shows the relationship between the wear durability and the dopant concentration of Au-, Pd-, and Pt-doped carbon films evaluated by the AFM nanowear test. The durability of Pt-C degraded with an increase in the Pt concentration. The wear durability depth abruptly increased at a Pt concentration of 15 at.%. However, the wear characteristics of Au-C and Pd-C differ from that of Pt-C. The wear durability of Au-C and Pd-C showed a slight change when the metal concentration was increased to 15-16 at.%.

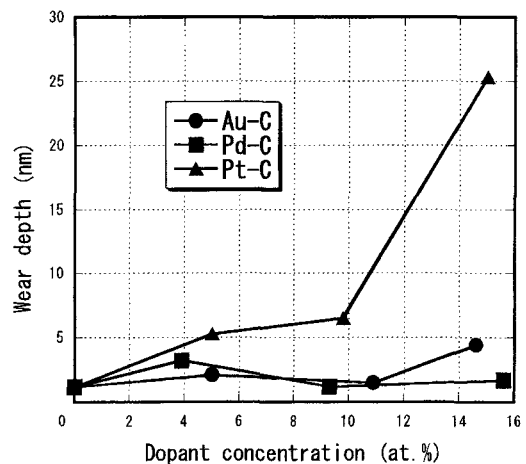


Fig. 3 Relationship between wear durability and dopant concentration of Au-, Pd-, and Pt-doped carbon films

3.4 Carbon 1s spectra analysis by XPS of the films

We analyzed the XPS carbon 1s spectra of the doped and non-doped films and separated the spectra into the components of C-C sp³, C-C sp², and C-O bondings. Since the C-O component is small, we defined the sp³ fraction as the sp³ component divided by the sum of the sp³ and sp² components ($I_{sp^3}/(I_{sp^3}+I_{sp^2})$). Figure 4 shows the relationship between the sp³ fraction and the dopant concentration of Au-, Pd-, and Pt-doped carbon films.

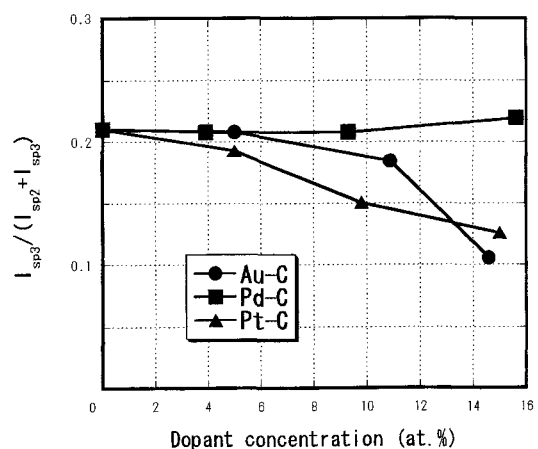


Fig. 4 Relationship between sp³ fraction and dopant concentration of Au-, Pd-, and Pt-doped carbon films

The sp^3 fraction of Au-C and Pt-C decreased with an increase in the dopant concentration, however, the dopant concentration of Pd-C was almost the same regardless of the Pd concentration.

In general, the sp^3 component decreases in non-hydrogenated carbon films cause the resistivity decrease and the degradation of the wear durability. The resistivity of Pt-C decreased and its wear durability degraded as the Pt concentration increased. The Pt concentration dependency of the resistivity and wear durability characteristics corresponds to that of sp^3 fraction changes. Furthermore, the resistivity and wear durability of Pd-C was almost the same regardless of the Pd concentration. These characteristics of Pd-C correspond to the unchanged sp^3 fraction of Pd-C with an increase of the Pd concentration. In the case of Au-C, the sp^3 fraction decreased with increasing Au concentration, however, the resistivity and wear durability showed almost the same characteristics regardless of the Au concentration. The resistivity and the wear durability of Au-C did not correspond to the sp^3 fraction changes with an increase in the Au concentration. Detailed investigations on the relationship between the microscopic structure of the Au-, Pd-, and Pt-doped carbon films and the resistivity and wear durability characteristics of the films are the subjects of future work.

4. CONCLUSION

We deposited Au-, Pd- and Pt-doped carbon films onto silicon substrates using a RF sputtering method and evaluated the morphology, resistivity, wear durability and carbon sp^3 and sp^2 fraction of the deposited films. The results are as follows:

1) The resistivity of the Pt-doped carbon film decreased and its wear durability degraded with an increase of the Pt concentration. The Pt concentration dependency of

the resistivity and the wear durability characteristics corresponds to that of the sp^3 fraction.

2) The resistivity and the wear durability of the Pd-doped carbon film were almost the same regardless of the Pd concentration. These characteristics of Pd-doped carbon film correspond to the unchanged sp^3 fraction of Pd-C with an increase of the Pd concentration.

3) The sp^3 fraction of the Au-doped carbon film decreased with an increase of the Au concentration, however, the resistivity and wear durability were almost the same regardless of the Au concentration. The resistivity and the wear durability of Au-C did not correspond to the sp^3 fraction changes with an increase of the Au concentration.

References

- [1] A. Grill: *Wear*, 168 (1993) 143.
- [2] K. Schiffmann: *Wear*, 216 (1998) 27.
- [3] T. Hayashi, S. Hirono, M. Tomita, and S. Umemura: *Nature*, 381(1996), 772.
- [4] K. Hayashi, T. You, O. Niwa, M. Tomita, and S. Hirono: *Proc. 34th Chemical Sensor Symposium*, 1L32, Sept. 12-13, 2002.
- [5] S. Matsuhashi, S. Umemura, S. Hirono, S. Suzuki, and R. Kaneko: *Abstracts of FSE 2001*, A2-11, Oct. 28-Nov. 1, 2001.
- [6] B. N. Chapman: *Glow Discharge Processes, Sputtering and Plasma Etching*, John Wiley and Sons, Inc, New York (1980) Appendix 7.
- [7] A. Kinbara and H. Fujiwara: "Thin Films", *Syokabo*, Tokyo (1979) 250 (in Japanese).
- [8] R. Kaneko, S. Oguchi, T. Miyamoto, Y. Andoh, and S. Miyake: *STLE Special Publication*, SP-29 (1990) 31.
- [9] S. Umemura, Y. Andoh, S. Hirono, and R. Kaneko: *IEICE Trans. on Electronics*, E81-C (1998) 337.