PHYSICAL REVIEW B **69**, 193406 (2004)

Formation of carbon-gold-sulfide conductive granular molecules by a cooperation process of plasma CVD and sputtering

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(Received 12 January 2004; published 24 May 2004)

Carbon-gold-sulfide (C-Au-S) films formed by cooperation process of plasma chemical vapor deposition (CVD) and sputtering were studied by x-ray diffraction, electron spectroscopy for chemical analysis (ESCA) and refractive index measurement before and after thermal treatment at 200 °C for 30 min. The x-ray diffraction patterns of gold cluster in the film were not observed. The chemical shifts of ESCA spectra for C, Au, and S atoms were 2.90, 2.40, and 0.95 eV, respectively, and were changed little after the thermal treatment. The atoms are expected to be ionic-bonded to the granular molecule. The refractive index was changed little by the thermal treatment compared to the carbon-gold (C-Au) film. The thermally stable conductive granular molecule of C-Au-S was confirmed experimentally.

DOI: 10.1103/PhysRevB.69.193406 PACS number(s): 68.60.Wm, 77.84.Lf, 82.80.Pv, 73.21.La

I. INTRODUCTION

CS_2 and Te or Bi mixtures were first reported as a light recording substance, which was formed by a cooperation process of plasma polymerization of CS_2 and vacuum evaporation of Te or Bi.[1] For the film, a metal atom of Te or Bi was vaporized or crystallized by light irradiation. However, the real structure of metal atoms in the film has not been examined.

Metal-containing carbonaceous films were reported by many authers.[2–5] Gold (Au) atoms mixed with plasma polymerized films, which were formed by plasma polymerization of organic vapor and sputtering of gold discharge plate, were studied widely with special emphasis by Kay,[6] Biederman,[7] and Marutinu.[8] In the film, the gold atoms were mixed in the form of a cluster at a higher content of more than a few volume %, which had polycrystalline structure. For the film, Martinu[8] reported the refractive index at a gold atom content of 25 vol % to be 2.8.

Because the gold atom was expected to have a large electronic polarizability,[9] the gold atom containing carbonaceous film will show a large refractive index if the gold atoms are dispersed atomically in the film. To realize a uniform (atomically) distribution of gold atoms in the carbonaceous film, the gold atom was mixed with a carbon-sulfur mixture[10] because the sulfur can chemically bond with the gold atom.[11] In practical terms, a carbon-gold-sulfide (C-Au-S) film was formed by cooperation process of plasma chemical vapor deposition (CVD) and sputtering with a mixture of methane (CH_4), SF_6, and Ar gases using a gold (Au) plate discharge electrode. The carbon-sulfide film was deposited by plasma CVD of methane (CH_4) and a SF_6 and Ar mixture gas by HF dissociation reaction.[10]

The C-Au-S film was observed to be amorphous without gold polycrystalline clusters according to x-ray diffraction measurements.[12] For the film with gold content at a few at. %, the refractive index of the C-Au-S film showed a large value higher than 3.5,[9] which was larger than that obtained by Martinu.[8] However, the refractive index was observed to be decreased with increasing gold atom at a content more than 10 at. %.[12] This was an unexpected result. Why did the refractive index not increase simply with increasing gold atom content? One possible explanation might be the existence of the conductive C, Au, and S granular molecules in the insulating amorphous film, where the large electronic polarizability of gold will be concealed by the electronic cloud similar to the gold cluster.[8,12] In order to confirm the speculation, the chemical bonds and the thermal stability were studied by x-ray diffraction, ESCA, and refractive index measurement.

II. EXPERIMENT

The plasma CVD reactor has a parallel plate electrode of 20 cm diameter and a 1.5 cm gap between the electrodes. The upper electrode made of graphite was connected to a 13.56 MHz discharge power source, the lower electrode was grounded with the reaction vessel of stainless steel, and the CH_4, SF_6, and Ar mixture gas was introduced through the many small holes on the upper electrode. The gold plate measuring 5×5 cm^2 was set on the upper electrode, as mentioned in a previous paper.[12] The substrate for the deposition was glass and a Si wafer of Sb doped and $\langle 100\rangle$ oriented with 9.7° off with a resistance $<0.02\ \Omega$ cm. The C-Au-S films were formed at an argon flow rate of 10 and 15 SCCM (SCCM denotes cubic centermeter per minute at STP) with a fixed CH_4 and SF_6 flow rate of 10 SCCM at a pressure of 0.07 Torr, a discharge power of 100 W, a deposition duration of 30 min, and a discharge frequency of 13.56 MHz. In order to compare the properties, carbon-gold (C-Au) films were formed by the same reactor at same deposition conditions with a mixture gas of methane and Ar.

Thermal treatment of C-Au-S films was performed using an oven, which can be heated from a room temperature up to 400 °C and the temperature can be maintained automatically at a fixed value. The thermal treatment duration was 30 min at a temperature of 200 °C, then the samples were cooled down to a room temperature in the air. X-ray diffraction spectra, ESCA, and refraction index measurement of the

TABLE I. Atomic compositions and the refractive index *n* of the C-Au film (pressure 0.07 Torr).

Flow of Ar (SCCM)	Atomic composition C (%)	Au (%)	O (%)	*n*
10	93.4	6.5	0.1	3.0
15	87.6	12.3	0.1	2.9

TABLE II. Atomic compositions and the refractive index of the C-Au-S film (pressure 0.07 Torr).

Flow of Ar (SCCM)	Atomic composition C (%)	S (%)	Au (%)	F (%)	O (%)	*n*
10	86.8	2.6	10.5	0.0	0.1	2.5
15	86.7	3.6	9.5	0.1	0.1	3.3

films were performed using an x-ray diffractometer (Rigaku, Rint 200), ESCA apparatus (VG Sci., ESCALAB 210), and ellipsometer (Plasmos, SD Ellipsometer) at 633 nm, respectively, before and after thermal treatment.

III. RESULTS AND DISCUSSIONS

The thicknesses of the films are approximately 600–800 nm. The atomic compositions of each sample were evaluated from the ESCA measurement after cleaning the sample surface by Ar sputtering for 1 min. Atomic composition and refractive index of C-Au and C-Au-S films are shown in Tables I and II, respectively.

X-ray diffraction (XRD) spectra for the C-Au film before and after the thermal treatment are shown in Fig. 1. Except for the diffraction peak of the Si wafer at $2\theta = 56.17°$, the diffraction peaks at $2\theta = 38.2°$, $2\theta = 44.4°$, $2\theta = 64.6°$, and 77.6°, which relate to the Au polycrystalline cluster,[12] became more narrow peaks from the broad peaks. This change will be referred to as the change of the cluster structure of gold. The gold cluster size was changed from 2.3 to 8.6 nm due to thermal treatment, which was evaluated using the classical Scherrer formula.[13]

X-ray diffraction spectra for the C-Au-S film before and after the thermal treatment are shown in Fig. 2, where the films were formed at a CH_4, SF_6, and Ar flow rate of 10 SCCM, and the atomic compositions were 86.8, 2.6, and 10.5 for C, S, and Au, respectively. The diffraction peak of the Au cluster at $2\theta = 38.2°$, $2\theta = 44.4°$, $2\theta = 64.6°$, and 77.6° could not be distinguished for both samples before and after the thermal treatment. Therefore, it is concluded that a gold cluster larger than a few nanometers was not observed in the C-Au-S film.

ESCA spectra of the C-Au and C-Au-S film were also measured before and after the thermal treatment. It is well known that ESCA peaks for each atom are observed at a deviated energy from the original energy if the atoms are ionic-bonded and/or grouped with charged particles.[14] Its deviated energy difference is known as a chemical shift. The chemical shifts were measured for two samples before and after the thermal treatment, as shown in Tables III and IV,

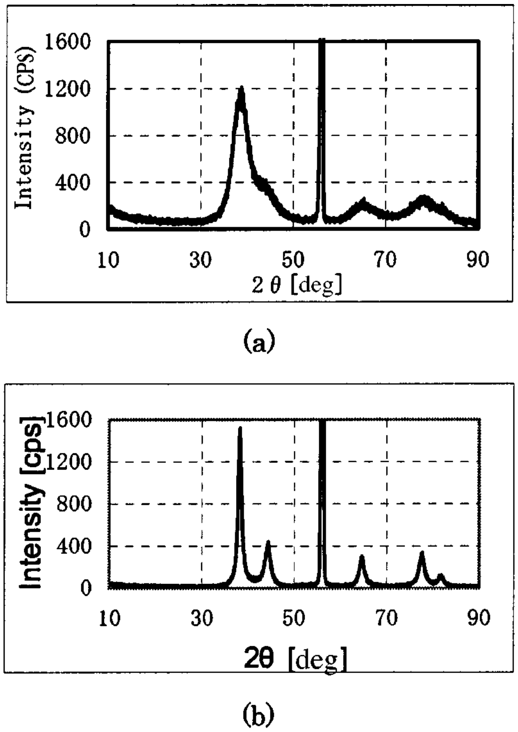

FIG. 1. XRD spectra of C-Au films carried out by a Cu *Kα* radiation source; pressure 0.07 Torr; Au, 12.3 at.%. (a) As deposited. (b) After annealing.

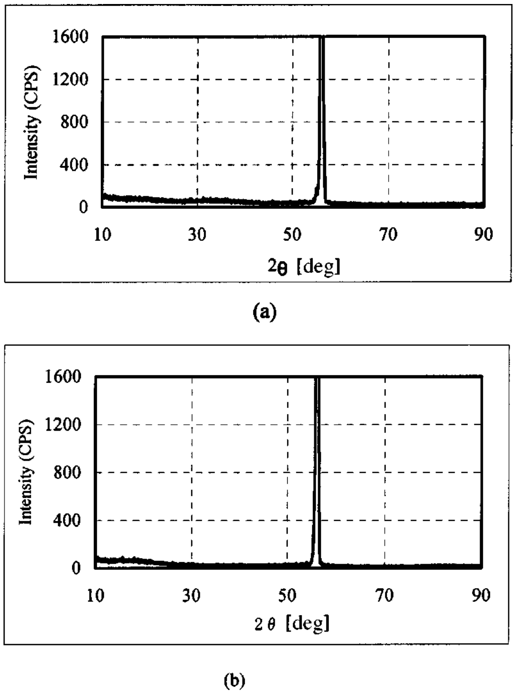

FIG. 2. XRD pattern of the C-S-Au film carried out by a Cu *Kα* radiation source; pressure 0.07 Torr; Au, 10.5 at.%. (a) As deposited. (b) After annealing.

TABLE III. Chemical shift of the C-Au film. Deposition conditions: CH_4, 10 sccm; pressure: 0.07 Torr.

Ar flow rate (SCCM)	As prepared		After annealing 30 min at 200 °C	
	Chemical shift (eV)		Chemical shift (eV)	
	C (284.6)	Au (84)	C (284.6)	Au (84)
10	0.90	0.45	0.53	0.35
15	0.45	0.25	0.40	0.12

TABLE V. Refractive index of the film; deposition pressure 0.07 Torr.

Ar flow rate (SCCM)	C-Au film		C-Au-S film	
	As prepared	After annealing	As prepared	After annealing
10	3.0	2.8	2.5	2.5
15	2.9	2.6	3.3	3.2

respectively. The original binding energy of core electron for each atom is also indicated in the tables. All of the atoms showed positive chemical shift. The measured values of chemical shift were scattered largely for the C-Au film as 0.9 and 0.45 for C. The reason for this will be referred to as the condition of sample preparation.

The effects of thermal treatment on the chemical shift were different for two kinds of samples. For the C-Au film, the obtained values of chemical shift were relatively small but the changing ratios were large after the thermal treatment. Actually the chemical shifts of carbon and gold atom formed at 10 SCCM of Ar flow rate were 0.90 and 0.45 eV, respectively. However, they were changed to 0.53 and 0.35 eV, respectively, after the thermal treatment.

On the other hand, the values of chemical shift for the C-Au-S film formed at 10 SCCM of Ar flow rate were relatively large compared to the C-Au film. The chemical shift of C, S, and Au were 2.90, 2.40, and 0.95 eV, respectively, and the chemical shifts were changed to 2.50, 2.10, and 0.80 eV after the thermal treatment. However, the variation caused by the thermal treatment was relatively small compared to the C-Au film. The small changing ratio of chemical shift means the main chemical bond of C-Au-S was maintained after the thermal treatment up to 200 °C. From the chemical shift measurement for C, Au, and S atoms, it is supposed that the atoms are grouped under a relatively large electronic field as a granular molecule.

The refractive indices for the C-Au and C-Au-S film were also measured before and after the thermal treatment by an ellipsometer, as shown in Table V. The refractive index of the C-Au film was 3.0 and 2.9 for two samples, and then the values were decreased to 2.8 and 2.6, respectively, after the thermal treatment. On the other hand, the refractive indexes of 2.5 and 3.3 for the C-Au-S film were almost same as 2.5 and 3.2 after the thermal treatment.

According to the dielectric theory,[15] a polarization catastrophe was observed for the C-Au film at a gold atom content higher than 10 at. % because the electronic polarizability of gold is very large.[9,10,12] However, the gold atoms in the polymeric and amorphous carbon film at a content of more than 10 at. % form a polycrystalline cluster and the cluster is conductive. Therefore, the clusters operate as a large atom because the electronic polarization is concealed by the electronic cloud in the cluster. Then the refractive index was limited to about 3. On the other hand, the scenario must be different for the C-Au-S film because the gold atoms are expected to be distributed more uniformly (atomically) compared to the C-Au film. However, the refractive index was not increased remarkably. From the observation of the ionically bonded C-Au-S molecule, it is supposed that the film contains a conductive granular molecule with 0.4–0.6 nm diameter where 2 or 3 gold atoms are included in the conductive molecule from the refractive index analysis.[12] The conductive granular molecule was also observed by the atomic force microscopy–scanning tunneling microscopy method.[16]

IV. CONCLUSION

A C-Au-S film with a gold atom content of 10.5 at. % was thermally treated at 200 °C for 30 min. Before and after the treatment, x-ray diffraction, ESCA, and refractive index measurements were performed on the film. The x-ray diffraction patterns, the chemical shift of ESCA spectra, and the refractive indices were changed little compared to the C-Au film. From the large chemical shift for the C, Au, and S atoms in the C-Au-S film, the C, Au, and S atoms are expected to be ionic-bonded in the conductive granular molecule. Therefore, it is supposed that the C-Au-S conductive granular molecule will work as a quantum dot because the size is expected to be sub-nanometer.

TABLE IV. Chemical shift of the C-Au-S film. Deposition conditions: CH_4, 10; SF_6, 10 sccm; pressure: 0.07 Torr.

Ar flow rate (SCCM)	As prepared			After annealing 30 min at 200 °C		
	Chemical shift (eV)			Chemical shift (eV)		
	C (284.6)	S (164)	Au (84)	C (284.6)	S (164)	Au (84)
10	2.90	2.40	0.95	2.50	2.10	0.80
15	2.93	2.20	0.90	2.70	2.00	0.74

ACKNOWLEDGMENTS

Part of this work was performed at the Center of Cooperative Research in Advanced Science and Technology, Nagoya University. We express our great thanks to the related persons. A part of this work was performed under the 21st Century COE Program by the Ministry of Education, Culture, Sports, Science and Technology in Japan.

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[1] Yoshihiro Asano, Hiroki Yamazaki, and Akira Morinaka, Jpn. J. Appl. Phys., Part 1 **22**, 480 (1983).

[2] *Techniques and Applications of Plasma Chemistry*, edited by J. R. Hollahan and A. T. Bell (Wiley Interscience, New York, 1974).

[3] *Thin Film Processes*, edited by J. L. Vossen and W. Kern (Academic Press, New York, 1978).

[4] H. Yasuda, *Plasma Polymerization* (Academic Press, New York, 1985).

[5] *Plasma Deposition, Treatment, and Etching of Polymers*, edited by Riccardo d'Agostino (Academic Press, San Diego, 1990).

[6] E. Kay, Z. Phys. D: At., Mol. Clusters **3**, 251 (1986).

[7] H. Biederman, Vacuum **37**, 367 (1987).

[8] L. Martinu, Sol. Energy Mater. **15**, 21 (1987).

[9] M. Matsushita, Md. Abul Kashem, and S. Morita, Thin Solid Films **407**, 50 (2002).

[10] Md. Abul Kashem, Masaki Matushita, and S. Morita, J. Photopolym. Sci. Technol. **15**, 317 (2002).

[11] K. Ishikawa, T. Isonaga, S. Wakita, and Y. Suzuki, Solid State Ionics **79**, 60 (1995).

[12] Md. Abul Kashem, Masaki Matushita, and Shinzo Morita, Jpn. J. Appl. Phys., Part 2 **43**, L355 (2004).

[13] C. W. Bunn, *Chemical Crystallography* (Oxford University Press, London, 1961).

[14] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Eden, K. Hamrin, U. Gelous, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1969).

[15] Charles Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1985), p. 379.

[16] Mikinori Suzuki, Md. Abul Kashem, and Shinzo Morita, IEICE Trans. Electron. **E87-C**, 179 (2004).