Synthesis of Antimony Doped Amorphous Carbon Films

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Abstract. We report the effects of antimony (Sb) doping on the electrical and optical
properties of amorphous carbon (a-C:H) films grown on silicon and copper substrates by
magnetron sputtering deposition. For film deposition, the mixture targets fabricated from
carbon and antimony powders was used. The atomic concentration of carbon, hydrogen, and
antimony, in the film deposited from the 1.0 mol% Sb containing target were 81, 17, 2 at.%,
respectively. These elements were homogeneously distributed in the film. On the structural
effect, the average continuous sp² carbon bonding networks decreased with Sb concentration
increasing, and defects in the films were increased with the Sb incorporation because atomic
radius of Sb atoms is twice larger size than that of carbon. The optical gap and the electrical
resistivity were carried out before and after the Sb doping. The results show that optical gap
dropped from 3.15 to 3.04 eV corresponding to non-doping to Sb-doping conditions,
respectively. The electrical resistivity reduced from 10.5 to 1.0 MΩm by the Sb doping. These
results suggest the doping level was newly formed in the forbidden band.

1. Introduction
Silicon has been used as primary material for electronic devices. Carbon and silicon are the
homologous element at 14th group and one of the crystalline carbon materials is diamond. Diamond
with energy band gap of 5.5 eV is an attractive semiconductor which can be applied to next generation
of electronic devices [1,2]. As amorphous silicon is used for one of the electronic material, an
amorphous carbon (a-C:H) has potential for the material for the electronic devices. Some studies were
reported about electronic properties on a-C:H materials. For example, Saitoh et al. reported field
emission properties of the nitrogenated a-C:H films deposited on a sharp tip of ZnO [3]. And some
researcher also reported devices using a-C:H films [4-6].
Most of such study, dopant for the a-C:H materials is nitrogen [6-8]. Conway et al. presented that
doping effect of nitrogen doping on a-C:H films [8]. Omer et al. reported photovoltaic characteristics
on the device of a-C:H films on the silicon substrate [6]. On silicon technology, nitrogen is not
primary dopant to obtain n-type semiconductors. Phosphor (P) or antimony (Sb) has been used to
doping for silicon to obtain the n-type semiconductor. The investigation for P doping for a-C:H films
was already reported [9-11], but no one reported the investigation of Sb doping effect for a-C:H films.
In this study, Sb-doped a-C:H films were synthesized to understand doping effect on a-C:H materials.
2. Experimental

Sb-doped $a$-C:H films were deposited from the carbon and antimony mixture target by sputtering with Ar plasma. Targets for the deposition were prepared by the compression moulding from powder mixtures. Sb concentrations in these powder mixtures were coordinated to 0.1, 0.3, 0.5, and 1.0 mol%. The target was fixed to a cathode connected to a high-voltage pulse power supply. The purity and the flow rate for Ar were 99.99% and 20 cm$^3$/min. The pressure was controlled at 1.0 Pa during deposition, and the deposition time was set at 120 min. The pulse voltage, frequency and width were -1 kV, 20 kHz and 5 $\mu$s, respectively. Substrates used were Corning #7059 glass, pure copper plate, silicon (100). The distance from the substrate to the target was approximately 10 cm.

The $a$-C:H film structure was also evaluated using an Raman spectroscope equipped with an Ar laser light source of 514.5 nm wavelength (NRS-1000: JASCO). The peaks in the Raman spectra of different $a$-C:H films were separated by curve fitting using Gaussian functions to obtain the integrated intensity ratio $I_D/I_G$ and G peak position. The composition in each $a$-C:H film was evaluated by the Rutherford backscattering spectrometry (RBS) and the elastic recoil detection analysis (ERDA) using a He$^+$ ion beam (Nissin High Voltage: NT-1700HS). The elemental distribution in the thickness direction of the $a$-C:H films was estimated by the glow discharge optical emission spectroscopy (GD-OES HORIBA / JOBIN YVON: JY - 5000RF). Optical properties of the deposited $a$-C:H films were investigated using the #7059 glass substrate in the wavelength range from 300 to 1900 nm. The optical band gap ($E_g$) of the $a$-C:H film was derived from the extrapolation of the linear parts of curve at 0 using the Tauc relation. Electronic defects in the $a$-C:H films were investigated by electron spin resonance spectroscopy (ESR).

3. Results and Discussion

First, the composition of the Sb doped $a$-C:H film deposited from the 1.0 mol% Sb containing target was determined by the RBS/ERDA measurement. The contents of film were 81, 17, 2 at.% for carbon, hydrogen, and antimony, respectively. Figure 1 shows the time dependence of the optical emission intensities for each element as results of GD-OES for the Sb doped $a$-C:H film deposited from 1.0 mol% Sb containing target. The distribution of Sb in the film was relatively-uniform, and the deposited film consisted of carbon and antimony.

Figure 2 shows the Raman spectra of the films which contained each Sb concentration. The Raman spectra of $a$-C:H films show the G (graphitic)-band around 1550 cm$^{-1}$ and the D (Disorder)-band around 1350 cm$^{-1}$, indicating that films are amorphous carbon. The intensity of the G-band decreases as the Sb concentration in the target increases. These results indicate that the average size of the $sp^2$ cluster consisting of the continuous bonding of $sp^2$ carbon in $a$-C:H films depends on the Sb concentration in the target. The G-band and D-band were fit assuming a Gaussian distribution, and the ratio of peak areas on D and G band, $I_D/I_G$, was calculated as shown in Figure 3. $I_D/I_G$ increases with increasing of the Sb concentration in the target. It is generally assumed that the lower the $I_D/I_G$ ratio of the $a$-C:H is the longer average continuous $sp^2$ carbon bonding networks exists.
The variation of $E_g$ as a function of the Sb concentration in the target increases is shown in Figure 4. $E_g$ for the $a$-C:H films decreases with increasing of the Sb concentration. $E_g$ is as large as 3.15 to 3.04 eV, indicating that these $a$-C:H films are semiconductors. Robertson et al. proposed to obtain the average $sp^2$ carbon cluster size in $a$-C:H films from $E_g$ using the equation: $E_g = \frac{0.77}{L_a}$, where $L_a$ is the $sp^2$ bonding cluster size [12]. As this relationship using Figure 4, the $sp^2$ cluster size in the films for films deposited from 0 and 1.0 mol.% Sb doped target was approximately 0.24 and 0.25 nm, respectively. This trend is not matched with the dependence of $I_D/I_G$ calculated from results of Raman measurements. From results of Raman measurements, the $sp^2$ cluster size decreasing with the Sb concentration increasing suggests that the size of $sp^2$ cluster was limited by doped Sb. Raman measurements can only measure carbon atom networks, not estimate Sb. Hence that mismatch suggests that doped Sb make the localized state in its band gap, and appear the leading of the decreasing of band gap. It was also considered Sb doping into the 14th group element brought the formation of the new energy level in the band gap, and effected the reducing of the band gap.
Defect densities in the $a$-C:H films increased with the increasing of Sb concentration in the target, as shown in Figure 5. Defect density was increased with the incorporation of Sb. Because atomic radius of Sb atoms is twice larger size than that of carbon, it was considered that unpaired electron of carbon atoms increased around Sb atoms.

![Figure 5. Defect density vs. Sb content in the target.](image)

The depletion of the electrical resistivity was found when Sb concentration increased, as shown in Figure 6. The electrical resistivity of the $a$-C:H film rapidly reduced by 0.1 mol% Sb addition to the target. This rapid reducing indicated the formation of new energy level in the band gap by Sb doping. After that, the electrical resistivity was moderately decreased with the Sb concentration increase. The electrical resistivity became approximately 1.0 MΩm at the film deposited from 1.0 mol% Sb contained target. The decrease of the electrical resistivity by the incorporation of Sb was caused by this new band formation, but was also caused by the increasing of $sp^2$ cluster size.

![Figure 6. Electrical resistivity vs. Sb concentration in the target.](image)

4. Conclusions
Sb doped $a$-C:H films were synthesized, and the effect of the Sb doping on the electrical and optical properties was investigated. On the Sb doped $a$-C:H deposited film from the 1.0 mol% Sb containing target, the atomic concentration of carbon, hydrogen, and antimony were homogeneously distributed at 81, 17, 2 at.%, respectively. By the Sb incorporation, the average of network size of continuous $sp^2$ carbon bonding decreased and defect densities were increased. Sb doping reduced the optical gap from 3.15 to 3.04 eV, and the electrical resistivity from 10.5 to 1 MΩm. These results suggested the doping level was newly formed in the forbidden band.
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6. References
[1] Koide Y 2004 Dia. Relat. Mater. 13 1963
[2] Hirama K, Miyamoto S, Matsudaira H, Yamada K, Kawarada H, Chikyo T, Koinuma H, Hasegawa K and Umezawa H 2006 Appl. Phys. Lett. 88 112117
[3] Saitoh H, Akasaka H, Washio T, Ohkawara Y, Ohshio S and Ito H 2002 Jpn. J. Appl. Phys. 41 6169
[4] Miyajima Y, Shkunov M and Silva S R P 2009 Appl. Phys. Lett. 95 102102
[5] Silva S R P and Carey J D 2003 Dia. Relat. Mater. 12 151
[6] Omer A M M, Rusop M, Adhikari S, Adhikary S, Uchida H and Umeno M 2005 Dia. Relat. Mater. 14 1084
[7] Bhattacharyya S, Walzer K, Hietschold M and Richter F 2001 J. Appl. Phys. 89 1619
[8] Conway N M J, Milne W I and Robertson J 1998 Dia. Relat. Mater. 7 1477
[9] Pearce S R J, Filik J, May P W, Wild R K, Hallam K R and Heard P J 2003 Dia. Relat. Mater. 12 979
[10] Kuo M T, May P W, Gunn A, Ashfold M N R and Wild R K 2000 Dia. Relat. Mater. 9 1222
[11] Regan E M, Uney J B, Dick A D, Zhang Y, Yanez J N, McGeehan J P, Claeyssens F and Kelly S 2010 Biomaterials 31 207
[12] Robertson J 1992 Surf. Coat. Tech. 50 185