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Comparative study of optical properties of germanium carbon films deposited by reactive sputtering and co-sputtering

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ABSTRACT

Amorphous hydrogenated germanium carbon (a-$Ge_{1-x}C_x$:H) films were prepared by both reactive sputtering of a pure Ge target in CH_4+H_2+Ar mixture and co-sputtering of Ge/Graphite target in H_2+Ar mixture. Their composition, chemical bonding and optical properties were investigated and through comparison it is found that the deposition rate of the films deposited by reactive sputtering is considerably larger than that deposited by co-sputtering. Moreover, the optical gap of the a-$Ge_{1-x}C_x$:H films deposited by reactive sputtering is lower compared with that of co-sputtering at the same C content which is mainly due to the relatively low content of Ge–C bonds that the co-sputtering fabrication process is more favorable to form the Ge–C bonds than reactive sputtering. Besides, the refractive index of the films appears as the similar rule of the optical band gap both due to the content of Ge–C bonds and the density of the films. Through the analysis of X-ray photoelectron spectroscopy (XPS), it is found that the formation of Ge–C bonds in the films is promoted by high energy C sputtered from graphite target.

1. Introduction

Researches on group IV amorphous semiconductors with relatively narrow optical band gap ($Eo<1.5$ eV) have attracted considerable attentions as an absorber material for bottom layer of a tandem solar cell. There have been many reports on a-SiGe:H and a-SiC:H films [1–3], whereas a-GeC:H films have attracted less attention for applications in optoelectronics [4] though they are being widely researched for their uses in infrared optics [5,6]. However, a-$Ge_{1-x}C_x$:H films may provide an apparently tunable band gap over a very wide range, which is important for photovoltaic applications [4,7,8]. Besides, due to its high absorption coefficient, a-$Ge_{1-x}C_x$:H needs much thinner layer than silicon to absorb most of solar photons, which means not only less manufacturing cost but also high efficiency of the solar cell [9]. Up to present, some optical, electrical, mechanical and structural properties have already been reported for a-$Ge_{1-x}C_x$:H films prepared by using different techniques, such as chemical vapor deposition [10–13], electron cyclotron resonance plasma processing [14], all of which can get a high quality film but relatively low deposition rate. For preparing a-$Ge_{1-x}C_x$ films with relatively high deposition rate, usually reactive sputtering of either germanium in hydrocarbon atmosphere [15–17] or mixed germanium/carbon targets in hydrogen and/or argon atmosphere [18–20] is used. However, there have been few reports about the comparative investigation of the a-$Ge_{1-x}C_x$:H films deposited by reactive sputtering of germanium in hydrocarbon atmosphere and co-sputtering of mixed germanium/carbon target in hydrogen and argon atmosphere.

In the present article, amorphous hydrogenated germanium carbon (a-$Ge_{1-x}C_x$:H) films are prepared by radio frequency (RF) reactive sputtering of germanium target in hydrocarbon atmosphere and mixed Ge/Graphite target in hydrogen and argon atmosphere, respectively. And the composition, chemical bonding and optical properties of the films fabricated by two different processes as a function of C content (x_c) are investigated.

2. Experimental details

Amorphous $Ge_{1-x}C_x$:H films were deposited on quartz substrates (fused silica of thickness 1 mm) and single crystal Si (100) (thickness 0.4 mm) by RF reactive sputtering of a single crystal Ge (111) target (Ø60mm×5 mm) in mixed discharge gasses of Ar(99.999%), CH_4 (99.99%) and H_2(99.99%) and mixed Ge/Graphite target in gasses of Ar and H_2. The mixed Ge/Graphite target was obtained by pasting several graphite targets (Ø10mm×1 mm) on Ge target (Ø60mm×5 mm). The distance between the target and the substrate was fixed at 80 mm and the chamber was evacuated by a turbomolecular pump to 8.0×10^{-5} Pa prior to film deposition. Before being introduced into the vacuum chamber, the quartz and Si substrates were cleaned ultrasonically in turn in acetone, ethanol and deionized water while the Si substrates were etched using hydrofluoric acid to remove oxide layer before cleaning. During the deposition process in both preparation techniques, the gas flow rate of Ar and H_2 was kept at 15 and 5 sccm (standard cubic centimeter per minute). In this paper, the only

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difference of the reactive sputtering and co-sputtering processes was the C source where its content is controlled by adjusting the flow rate of CH_4 in reactive sputtering process and the number of graphite targets on the Ge target in co-sputtering, respectively. For both deposition methods, the total gas pressure, substrate temperature and RF power were kept at 0.3 Pa, 250 °C and 70 W, respectively. To keep the pressure constant while the total gas flow rate was varied, a throttle valve was used.

X-ray diffraction was conducted for structure analysis of the films using Cu Kα radiation (40 kV, 45 mA) on X'Pert Pro MPD X-ray diffractometer. XPS measurements were performed for composition and bond character analysis using VG ESCALAB MKII X-ray photoelectron spectrometer with a monochromatized Al Kα (1486.6 eV) X-ray source. As the XPS measurements were not taken on line and the surface of the deposited films would adsorb CO_2 and O_2 in the air when the samples were taken out from the chamber, the deposited films were etched at an etching rate of 10 nm/min for 2 min before measurement to remove the adsorption layer on the surface. Optical transmittance over the wavelength range of 300–2500 nm was recorded by a UV-3150 Shimadzu UV–Vis–NIR double beam spectrophotometer and the optical band gap of the films were determined from the transmission spectra using the well-known Tauc equation. The thickness and the refractive index of the films at the wavelength of 632 nm were obtained by using a Uvisel Spectroscopic Ellipsometry system of JOBIN-YVON Company.

3. Results

The C content of all the samples fabricated by both different processes are obtained by XPS measurements. Although the content of hydrogen in the films cannot be obtained by XPS, the relative atomic concentration of C, x_c, and Ge in the films was unaffected and obtained from the computation of the sensitivity factors and peak areas of C_{1s} and Ge_{3d} using the formula $x_c = [C]/([C]+[Ge])$. Fig. 1 shows the deposition rate of the a-$Ge_{1-x}C_x$:H films as a function of the C content (x_c) deposited by reactive sputtering and co-sputtering. And the errors are mainly derived from the measurement errors of the ellipsometry and fitting residual errors induced by the choice of the dispersion formula. It is found that the deposition rate increases almost linearly with increasing x_c in the process of reactive sputtering while decreases for co-sputtering. Moreover, the deposition rate of the former is considerably higher than that of the latter's (22.8 nm/min and 1.2 nm/min at the C content about 15 at.% for reactive sputtering and co-sputtering respectively).

The optical gap *Eo* for the a-$Ge_{1-x}C_x$:H films as a function of the C content (x_c) is shown in Fig. 2 where the errors are mainly due to the assumption of the fixed reflectivity in Tauc equation. It is demonstrated from Fig. 2 that the optical gap *Eo* of the films deposited by both processes increases as the C content increases. Moreover, the optical gap of the a-$Ge_{1-x}C_x$:H films deposited by reactive sputtering is about 0.2 eV lower than that of co-sputtering at the same C content. The relationship between the refractive index and C content is shown in Fig. 3 and the errors of the refractive index are mainly derived from fitting residual errors induced by the choice of the dispersion formula. From Fig. 3 we found that the refractive index of the a-$Ge_{1-x}C_x$:H films deposited by co-sputtering is higher than that of reactive sputtering at the same C content which is similar to optical band gap. For both deposition techniques, the refractive index decreases against the increase in C content.

X-ray diffraction patterns of a-$Ge_{1-x}C_x$:H samples fabricated by two different processes are presented in Fig. 4, wherein (a) and (b) are deposited by co-sputtering with C content of 9.7 at.% and 18.32 at.% respectively and (c) and (d) are deposited by reactive sputtering with C content of 10.95 at.% and 16.82 at.% respectively. In Fig. 4, no diffraction peak is found for (c) and (d) while only a very broad diffraction peak (with a FWHM over 10°) is found for (a) and (b). So, all the samples fabricated by both different processes mainly have amorphous structure.

It is known that the optical gap and refractive index depend on the composition and structure of the films and all the samples fabricated by both different processes mainly have amorphous structure shown in Fig. 4. So the changes in the optical gap and refractive index of the a-$Ge_{1-x}C_x$:H films mainly depend on the composition and atomic bonding character of the films. Therefore XPS measurements are conducted further for purposes of characterizing the atomic bonding state in the films deposited both by reactive sputtering and co-sputtering. Fig. 5 shows the Narrow-scanning XPS of C_{1s} and the fitting results in which (a) is deposited by co-sputtering and (b) is deposited by reactive sputtering. It can be seen from Fig. 5 that the main features of both C_{1s} curves are their asymmetric shapes with small tails towards high binding energy. Therefore, the curves are well fitted into three peaks at 283.7, 284.4, and 285.2 eV, which can be ascribed to Ge – C, C – C, and C – H_n bond, respectively. The former relative content of the Ge – C bond is larger than that of the latter's while the relative content of the C – C bond of the former is lower than that of the latter's.

In order to investigate the relationship between chemical bonding and C content further, the relative integrated intensity of the Ge – C bond and C – C bond as a function of C content deposited by the two different processes are given in Figs. 6 and 7, wherein (a) is deposited by reactive sputtering and (b) is deposited by co-sputtering. And the errors are mainly derived from the Gauss fitting residual errors of the spectrums. It can be seen from Fig. 6 that the fraction of Ge – C bond

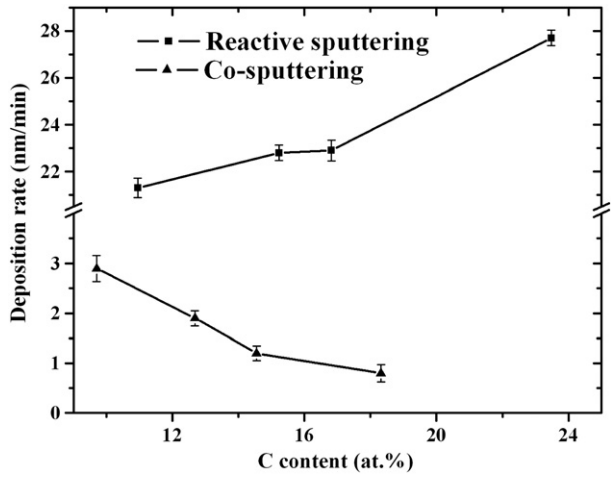

Fig. 1. The deposition rate of the a-$Ge_{1-x}C_x$:H films as a function of the C content deposited by reactive sputtering and co-sputtering.

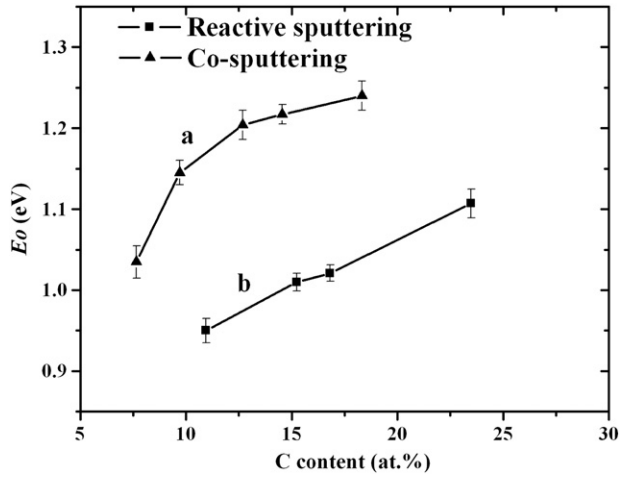

Fig. 2. The optical gap of the a-$Ge_{1-x}C_x$:H films as a function of the C content deposited by reactive sputtering and co-sputtering.