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Optical and electrical properties of nonstoichiometric a-$Ge_{1-x}C_x$ films prepared by magnetron co-sputtering

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ABSTRACT

Amorphous non-hydrogenated germanium carbide (a-$Ge_{1-x}C_x$) films have been prepared by magnetron co-sputtering method in a discharge of Ar. The dependence of structural and chemical bonding properties on the Ge/C ratio (R) has been investigated by X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy and Raman spectroscopy. The relationship between the chemical bonding and the optical and electrical properties of the a-$Ge_{1-x}C_x$ films has also been explored. It has been shown that the refractive index of the films increases from 2.9 to 4.4 and the optical gap decreases from 1.55 to 1.05 eV as R increases from 1.22 to 5.67. Moreover, the conductivity σ increases clearly and the activation energy E_a decreases with the increasing R owing to the reduction of sp^3 C—Ge bonds. The a-$Ge_{1-x}C_x$ films exhibit refractive index and optical gap values changing with x in a wide range, which may make a-$Ge_{1-x}C_x$ films good candidates in the fields of protection coatings for IR windows and electronic devices.

1. Introduction

Hydrogenated amorphous germanium (a-Ge:H) and its series of alloys, such as hydrogenated amorphous silicon germanium (a-SiGe:H), hydrogenated amorphous germanium carbide (a-$Ge_{1-x}C_x$:H) and amorphous germanium carbide (a-$Ge_{1-x}C_x$), have received considerable attention because of their exciting structural, optical, and electrical properties [1–4]. In particular, the refractive index of a-$Ge_{1-x}C_x$ may be adjusted by varying x in a wide range, which makes the films potential candidates for applications as multilayer anti-reflective and protective coatings of IR windows [5]. In addition, the band gap of the films can also be changed with x in a very wide range, which makes them good semiconductive material candidates in the design of electronic devices and photovoltaic cells [6]. Some optical, electrical and structural properties have already been reported for a-$Ge_{1-x}C_x$:H films prepared by the different techniques, such as activated reactive evaporation [7], plasma-enhanced chemical vapor deposition [8], reactive magnetron sputtering [9] and glow discharge [10]. However, so far, there are very few reports on amorphous non-hydrogenated germanium carbide (a-$Ge_{1-x}C_x$) films.

It is known that carbon atoms usually have sp^3 and sp^2 hybridizations in carbide films. The fractions of sp^3 and sp^2 hybridizations can be changed by Ge/C ratio (R), which could remarkably influence the optical and electrical properties of the films. Therefore, in this paper the chemical bonding and microstructural properties on a function of the Ge/C ratio of a-$Ge_{1-x}C_x$ films obtained by magnetron co-sputtering method in an argon atmosphere have been investigated by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. Finally, the intrinsic correlations between the chemical bonding properties and optical and electrical properties would be illustrated.

2. Experimental details

The a-$Ge_{1-x}C_x$ films were prepared by a RF (13.56 MHz) and DC magnetron co-sputtering method in a discharge of Ar (99.995%). Both of targets were 49 mm in diameter and 3 mm in thickness. One target was a single crystal pure germanium disk and the other was a graphite disk with a purity of 99.999%. The distance between the target and sample holder was fixed at 100 mm, and the base pressure in the chamber was about 2.0×10^{-4} Pa prior to film deposition. Before deposition, c-Si, glass and polished ZnS substrates were cleaned ultrasonically with acetone and alcohol, then were rinsed with de-ionized water, and finally were dried with high purity nitrogen.

The films were deposited at 200 °C. The Ar flow controlled using mass flow controller was kept at 40 sccm (standard cubic centimeter per minute) and the deposition pressure was always kept at 1.0 Pa. The summary of target powers is listed in Table 1. The films deposited on c-Si substrates were chosen for Spectroscopic

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Ellipsometry (SE), Raman and XPS measurements. The samples deposited on glass substrates were employed for electrical experiments. In order to avoid the strong absorption from c-Si, the films deposited on ZnS substrates were used for FTIR measurements.

The thickness of each film was obtained by measuring step heights using profilometry (Taylor Hobson FTS120-4616 profilometer). The XPS measurements were carried out by a PHI 5700 ESCA XPS instrument using a monochromatized Al Kα (1486.6 eV) X-ray source. Prior to XPS analyses, the argon ion-cleaning lasting 120 s was accomplished by 1.1 keV ion beam energy for all samples. During the measurement, the vacuum pressure was kept at about 10^{-6} Pa. The Raman measurements were performed in the range of 100–2000 cm^{-1} at room temperature with excitation provided by an argon laser operating at a wavelength of 458 nm. The incident laser power density was 0.226 W/cm^2 and the spectral resolution was 1 cm^{-1}. Infrared spectra in the 400–1600 cm^{-1} wave-number range were acquired using a PE-Spectrum One Fourier transform infrared spectrometer. A ZnS wafer was used as reference. The optical properties were analyzed by a Woollam Spectroscopic Ellipsometry system. The ellipsometeric data were recorded at the incidence angle of 70° in the spectral wavelength range 380–800 nm. The variation was analyzed on the refractive index (n) of the films at wavelength, λ = 632.8 nm. The square root of the product of absorption coefficient and photon energy is plotted against the photon energy and is extrapolated to calculate the band gap of all the films using the relation [11]:

$$(\alpha h\nu)^{1/2} = B^{1/2}(h\nu - E_g) \quad (1)$$

where B is a Tauc's constant and $h\nu$ is the incident photon energy, the absorption coefficient α is calculated from the extinction coefficient using the well known equation $\alpha = 4\pi k/\lambda$. The electric resistances of all films deposited on glass substrates were measured over the temperature range of 300–500 K by an electrometer (Keithley 617). Two parallel silver electrodes were provided by silver paste on the surfaces of samples before measurements.

3. Results and discussion

3.1. Composition and chemical bonding

The ratio between the germanium and carbon concentrations and deposition rate are listed in Table 1. The deposition rate increases from 14 to 47 nm/min with the increasing germanium target power (P_{Ge}). The germanium and carbon content are determined by XPS, and the absolute uncertainty is less than 10 at.%. The P_{Ge} dependence of the film composition is strong. The germanium content tends to increase gradually with increasing P_{Ge} from 43 to 162 W because the sputtering yield of germanium is promoted owing to the increase in the kinetic energy of argon ions with RF power.

Fig. 1 shows the FTIR spectra for the a-$Ge_{1-x}C_x$ films measured in a range of 400–1600 cm^{-1}, in which the main absorption bands at 610 cm^{-1}, 735 cm^{-1}, 1100 cm^{-1} and 1510 cm^{-1} are clearly observed. The absorption band at 610 cm^{-1} is related to the Ge–C stretching vibration [12]. This illustrates that some germanium atoms are combined with carbon atoms. The absorption band at 735 cm^{-1} is related to the Ge—C—C—C—Ge stretching vibration [13]. The absorption band around 1100 cm^{-1} may be due to sp^3 hybridized carbon in the film [13]. Additionally, the absorption band at 1510 cm^{-1} is attributed to graphite-like sp^2 carbon and disordered sp^2 carbon bands, which had become infrared active and shifted due to the incorporation of germanium atoms. Though the bondings in hydrogen-free diamond-like carbon films should normally be inactive in infrared vibrational modes, the infrared peaks like G band and D band in Raman spectra are activated because the germanium atoms replace some of the sp^2 carbon atoms position in films, the sp^2 C—C bond symmetrical vibrations is destroyed.

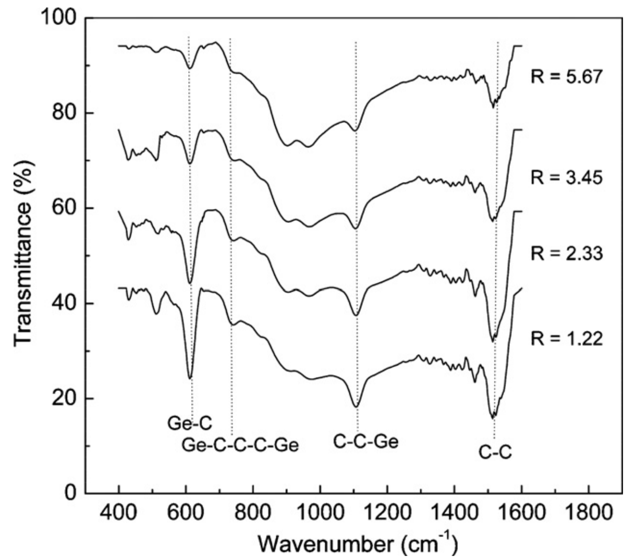

Fig. 1. FTIR spectra of the a-$Ge_{1-x}C_x$ films prepared with the different Ge/C ratios, in which the dash lines are just taken advantage to guide the eyes.

Raman spectra of the films in Fig. 2 show the features of characteristic a-$Ge_{1-x}C_x$: the typical amorphous germanium peak in a range from 80 to 350 cm^{-1} and the amorphous carbon peak in a range from 1200 to 1800 cm^{-1} which stems from the vibration of sp^2 carbon sites [14]. The C—Ge local vibration mode has been found at 530 cm^{-1} in epitaxial GeC alloys with carbon concentration below 7% and in $Ge_{1-y}C_y$ alloys by carbon implantation into germanium crystal [15]. However, in our work, no peak associated with C—Ge at 530 cm^{-1} or germanium nanocrystals at 300 cm^{-1} is observed in Raman spectra for any of the samples. No evident peak of sp^2 carbon sites is detected until R drops down to 1.22 in Raman spectra, which suggests an increasing sp^2-bonded carbon fraction is consorted with the carbon content in the films. The appearance of Ge—Ge (100–360 cm^{-1}) and C—C (1200–1800 cm^{-1}) peaks shows that the a-$Ge_{1-x}C_x$ film may contain the considerable clusters comprising carbon or germanium.

The inserts in Fig. 2 are Raman spectra obtained from germanium band and the carbon band of the a-$Ge_{0.55}C_{0.45}$ film. The region of 100–360 cm^{-1} is fitted with the germanium phonon vibrations at 130, 159, 220 and 275 cm^{-1} in Fig. 2(a). The vibrations at 130 cm^{-1} is still an uncertain mode which is found in amorphous germanium

Table 1
Deposition condition, germanium/carbon atomic ratio and deposition rate of a-$Ge_{1-x}C_x$ films.

Sample	P_{Ge} (W)	P_C (W)		Ge/C ratio	Deposition rate (nm/min)
		I_c (A)	U_c (V)		
a-$Ge_{0.55}C_{0.45}$	43	0.20	−500	1.22	13.8
a-$Ge_{0.67}C_{0.33}$	81	0.20	−500	2.33	30.6
a-$Ge_{0.77}C_{0.23}$	118	0.20	−500	3.45	41.4
a-$Ge_{0.95}C_{0.15}$	162	0.19	−520	5.67	46.8