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Effects of radio frequency power on the optical and electrical properties of germanium carbon films

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ABSTRACT

We have prepared amorphous hydrogenated germanium carbon (a-$Ge_{1-x}C_x$:H) films by radio frequency (RF) reactive magnetron sputtering and their composition, optical, electrical and chemical bonding properties are investigated as a function of RF power. The results show that the deposition rate increases and the optical gap of the a-$Ge_{1-x}C_x$:H films decreases as RF power increases from 30 to 90 W. The decrease of the optical gap is mainly due to the decrease in the carbon content. As increasing RF power, the refractive index of the films increases and the absorption edge shifts to long wavelength region. Besides, the room temperature dark conductivity increase with RF power is due to the decrease of the activation energy connected with the increase of Ge content. Through the analysis of X-ray photoelectron spectroscopy (XPS), we found that the formation of Ge–C bonds in the films is promoted by high RF power connected with relatively high self-bias and Ge content.

1. Introduction

Researches on the group IV amorphous semiconductors with relatively narrow optical band gap (E_o < 1.5 eV) have been aggressively investigated for use in hetero-structure devices and 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 it has been widely researched for uses in infrared optics [5–7]. However, a-$Ge_{1-x}C_x$:H films may provide apparently tunable band gap over a very wide range which is important for photovoltaic applications [4,8,9]. Besides, a-$Ge_{1-x}C_x$:H films can also provide a high absorption coefficient indicating that a-$Ge_{1-x}C_x$:H needs much thinner layer than silicon to absorb most of solar photons, which not only means less manufacturing cost but high efficiency of the solar cell [10]. 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 [11–14], plasma deposition processing [15,16], all of which can get a high quality film but relatively low deposition rate. In order to prepared a-$Ge_{1-x}C_x$:H films with a relatively high deposition rate, usually reactive sputtering technique [17–24] was used. However, so far, there have been very few reports about the effects of RF power on the optical, electrical and chemical bonding properties of a-$Ge_{1-x}C_x$:H films used as an absorber layer of solar cell [17,19].

As an absorber layer applied for a tandem solar cell, it is important and meaningful to investigate the optical and electrical properties of a-$Ge_{1-x}C_x$:H films. In the present article, amorphous hydrogenated germanium carbon (a-$Ge_{1-x}C_x$:H) films are prepared by RF reactive sputtering at different RF power and their optical and electrical properties, composition and chemical bonding have been performed by using spectrophotometer, high resistance meter and X-ray photoelectron spectroscopy (XPS).

2. Experimental details

Amorphous $Ge_{1-x}C_x$:H films are deposited on glass substrates (fused silica thickness 1 mm) and single-crystal Si (100) (thickness 0.4 mm) by RF reactive sputtering of a single crystal Ge (111) target (∅60 mm × 5 mm) in mixed discharge gases of Ar (99.999%), CH_4 (99.99%) and H_2 (99.99%). The films deposited on single-crystal Si substrates are used for the measurements of spectroscopic ellipsometry. The distance between the target and the substrate is fixed at 80 mm and the chamber is evacuated to 8.0×10^{-5} Pa prior to film deposition. Before being introduced into the vacuum chamber, the Si substrates are etched using hydrofluoric acid to remove possible oxide layer before cleaning and then all the glass and Si substrates are cleaned ultrasonically in turn in acetone, ethanol and deionized water. During the deposition process, the gas flow rate of Ar, CH_4 and H_2 are controlled by using mass flow controller and kept at 15, 5 and 5 sccm (standard cubic centimeter per minute). When the RF power was varied from 30 to 90 W, the total gas pressure and substrate temperature are kept at 0.3 Pa and 250 °C respectively.

X-ray diffraction is 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 are performed for composition analysis using VG ESCA LAB MKII X-ray photoelectron spectrometer with a monochromatized Al Kα (1486.6 eV) X-ray source. As the XPS measurements are not taken on line and the surface of the deposited films will adsorb CO_2 and O_2 in the air when the samples are taken out from the chamber, the deposited films are etched at an etching rate of 10 nm/min for 2 min before measurements to remove any adsorbed layer on the surface of the

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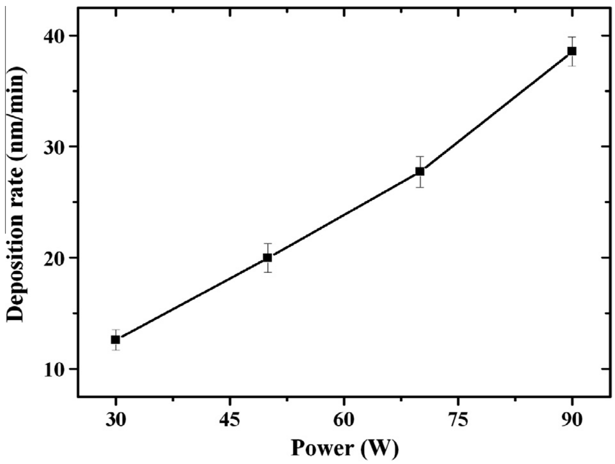

Fig. 1. The deposition rate of a-$Ge_{1-x}C_x$:H films as a function of RF power.

films. Optical transmittance over in the wavelength range of 400–1200 nm is recorded by a UV-3150 shimadzu UV–VIS–NIR double beam spectrophotometer and the optical band gap of the films are determined from the transmission spectra using the well-known Tauc's relation. The thickness and the refractive index of the films at the wavelength of 632 nm are obtained by using a Univsel Spectroscopic Ellipsometry system of JOBIN-YVON Company. The room temperature dark conductivity was measured on the amorphous films deposited onto glass substrates with evaporating coplanar Al ohmic electrodes and a 100 V applied voltage. The measurements use two points probe method and are performed using Agilent 4155C high resistance meter.

3. Results

Fig. 1 shows the deposition rate of the a-$Ge_{1-x}C_x$:H films as a function of RF power. It is demonstrated that the deposition rate increases almost linearly as RF power increases from 30 to 90 W. In Fig. 2, we show the transmission spectra of the a-$Ge_{1-x}C_x$:H films at the range of 400–1200 nm at different RF power. From Fig. 2 it could be found that the absorption edge shifts to long wavelength region (low energy) with the increase of RF power which means that the optical band gap decreases. As the absorption edge shifts to long wavelength region, the films have a good absorption property in the near-infrared waveband (1.2–1.6 eV) which will increase the utilization efficiency of sun light and improve the efficiency of the solar cell. The optical gap E_o for the a-$Ge_{1-x}C_x$:H samples are determined by plotting $(\alpha h\nu)^{1/2}$ against the photon energy $h\nu$ according to the Tauc equation. Fig. 3 shows the optical gap E_o and refractive index of the a-$Ge_{1-x}C_x$:H films as a function of RF power and it could be found from Fig. 3 that the optical gap decreases from 1.49 to 0.95 eV as RF power increases from 30 to 90 W, indicating that the a-$Ge_{1-x}C_x$:H films used as an absorber material of solar cell can be fabricated by changing the RF power. The refractive index of the a-$Ge_{1-x}C_x$:H films increases as RF power is increased. Besides, the values of self-bias U_s (V), thickness (d), optical gap (E_o) and refractive index (n) of the films deposited at different RF power are listed in Table 1. Fig. 4 shows the dark conductivity σ_d at room temperature (297 K) as a function of RF power for a-$Ge_{1-x}C_x$:H films and it could be found that the dark conductivity σ_d increases with increasing RF power.

Fig. 5 shows the carbon content (x) of the a-$Ge_{1-x}C_x$:H films determined by XPS measurements as a function of RF power. Although the content of hydrogen in the films cannot be obtained by XPS, the relative atomic concentration of C and Ge in the films is

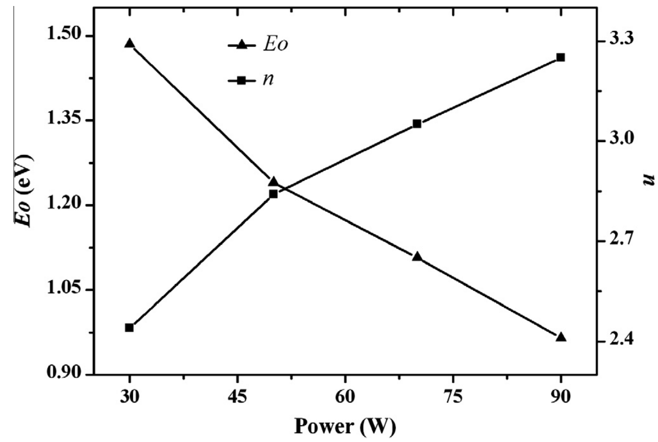

Fig. 3. The optical gap E_o and refractive index of a-$Ge_{1-x}C_x$:H films as a function of RF power.

Table 1
The values of self-bias U_s (V), thickness (d), optical gap (E_o) and refractive index (n) of the films deposited at different RF power.

	RF power (W)			
	30	50	70	90
Us (V)	140	190	230	270
d (nm)	1511	1498	1523	1464
E_o (eV)	1.49	1.24	1.11	0.95
n (632 nm)	2.44	2.74	3.05	3.25

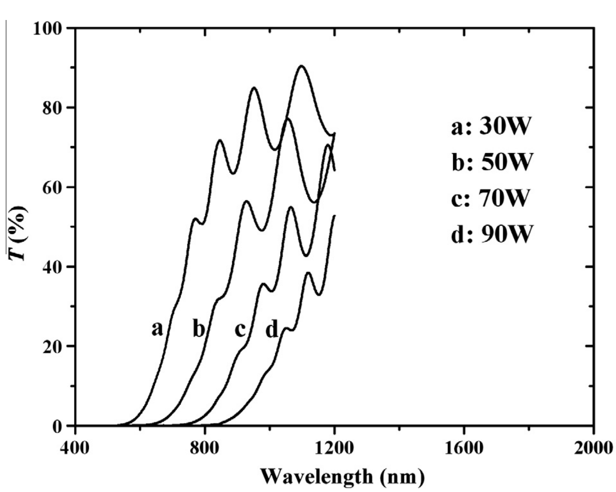

Fig. 2. The transmission spectrum of a-$Ge_{1-x}C_x$:H films with different RF power.

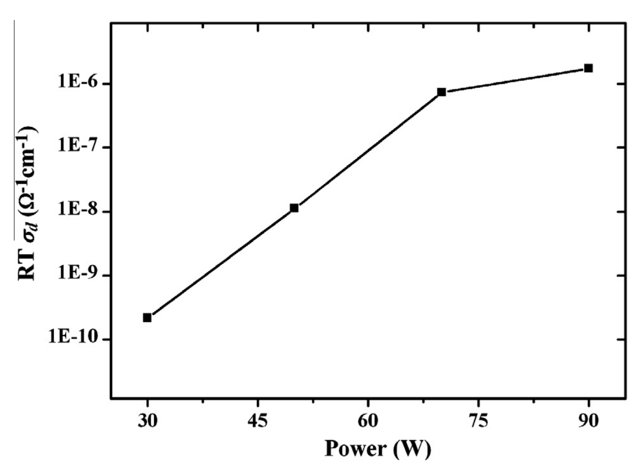

Fig. 4. The room-temperature dark conductivity of a-$Ge_{1-x}C_x$:H films as a function of RF power.