



Effect of substrate temperature and radio frequency power on compositional, structural and optical properties of amorphous germanium carbide films deposited using sputtering



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ABSTRACT

Fabrication of Ge_xC_{1-x} has been a big challenge because of the solubility of C in Ge. Only a small percentage of Ge—C bonds (11.6%) have been introduced so far. In this work, a-Ge_xC_{1-x} with GeC content up to 21% has been fabricated with 50 W RF power at 250 °C by reactive sputtering methods. The effects of the radio frequency power and substrate temperature on the yield of GeC were analysed in detail. The GeC percentage by volume was found to first increase and then decrease with increasing substrate temperature. Introduction of C into the Ge matrix seems to tune the optical bandgap over a range of 2.7 eV to 1.0 eV depending on the combination of substrate temperature and radio frequency power.

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1. Introduction

Germanium carbide thin films with narrow band gap ($E_g < 1.5$ eV) has been gaining considerable attention because of their remarkable structural, optical and electrical properties which make them promising candidates for applications in photovoltaics [1,2]. Tuneable band gap over a wide energy range is one of the particularly attractive features of this material [3,4]. Moreover, the absorption coefficient of germanium carbide film is much higher than that of Si and Ge [5]. This could make it a suitable candidate for the third generation photovoltaic cells such as the hot carrier solar cell [6] and as the bottom layer of tandem solar cells [7]. Other group IV alloys such as a-SiGe and a-SiC have been widely studied [8,9] whereas Ge—C gained much less attention in photovoltaic applications although they have been widely researched for their use as infrared windows. The optical, structural and compositional properties for Ge—C film synthesized under various conditions via reactive and co-sputtering [10–15], chemical vapour deposition [1], activated evaporation method [7,16], molecular beam epitaxy [17, 18] and reactive pulse laser deposition [19] have been reported. However, there have been few reports which discuss the actual Ge—C content in the deposited film [20,21]. Zhan et al. [20,21] demonstrated deposition methods of Ge_{1-x}C_x films by medium frequency magnetron reactive sputtering technique with a maximum 11.6% Ge—C content at a

bias voltage of 250 V and a maximum Ge—C content of 10.1% at a substrate temperature of 150 °C. To obtain a wide range of bandgap tunability and high conversion efficiency, a high percentage of GeC is desired in the film. In this article, amorphous germanium carbide films are prepared by radio frequency (RF) reactive sputtering of pure Ge and methane (CH₄) gas on Si (100) and quartz substrate. Variations of actual Ge—C content and band gap (E_g) with RF power and substrate temperature (T_s) were investigated.

2. Experiment and characterization

In this work, the Ge_xC_{1-x} films have been grown by RF (13.56 MHz) reactive sputtering of Ge target and CH₄ gas. The sputtering target consisted of a 4" Ge wafer with 99.999% purity. Before film deposition, the growth chamber was pumped down to below 10⁻⁴ Pa using a turbo-molecular pump. Films were grown simultaneously on Si (100) and quartz substrate to facilitate various characterization methods for structural, compositional and optical properties. Substrates were cleaned in Piranha solution and silicon substrates were dipped in hydrofluoric (HF) solution (10:1) to remove the native oxide layer before they were loaded into the growth chamber. Targets were pre-sputtered using Ar gas for 15 min prior to the deposition to remove any residual oxygen or impurities. During film depositions the substrates were heated up to 350 °C from room temperature. Films were deposited with two different RF powers, 40 W and 50 W, keeping the total gas (Ar + CH₄) pressure constant at 0.12 Pa using a mass flow controller. During the reactive sputtering, the C species mainly derived

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from the discharge of CH_4 near the growth surface. All deposited samples were amorphous, as revealed by X-ray diffraction patterns and showed good adhesion and stability on Si and quartz substrates.

Chemical composition of the films was determined by an ESCALAB250Xi XPS instrument using a mono-chromatic $\text{CuK}\alpha$ (0.15418 nm) X-ray source and uncertainty was less than ± 5 at.%. The films were etched for 60 s to eliminate the surface effect. Raman spectroscopy (Reinshaw, 514 nm) and glancing incidence x-ray diffraction (GIXRD) (Philips X'Pert Pro) using $\text{CuK}\alpha$ radiation were performed to study the phase and crystalline properties of the films deposited. Raman spectroscopy was performed in a range of 100–2200 cm^{-1} at room temperature with excitation provided by an argon laser operating at a wavelength of 514 nm. The validity of the position is 1 cm^{-1} . Dektak profilometer was used to measure the film thickness. GIXRD was conducted at a voltage of 45 kV and a current of 40 mA and using a $1/16^\circ$ divergent slit, a parallel plate collimator of 0.27° acceptance and a soller slit of 0.04 rad aperture. Optical transmittance over the wavelength range of 250–2000 nm was recorded using a spectrophotometer (PerkinElmer). Samples on silicon substrates were used for XPS and GIXRD and those on quartz slides were used for Raman spectroscopy and optical measurement.

3. Results and discussion

The compositions of the $\text{Ge}_x\text{C}_{1-x}$ films deposited under different conditions were characterized by XPS. Fig. 1 shows the variation of C1s and Ge3d atomic concentration with increasing substrate temperature (T_s) at constant RF power. Solid lines represent the C1s and dashed lines indicate the Ge3d atomic concentration. Black and red colours indicate the films deposited at 40 W and 50 W, respectively. During the synthesis of the $\text{Ge}_x\text{C}_{1-x}$ films, C species formed from discharge of methane and Ge atoms from the sputtering of Ge target provide C and Ge to the substrate respectively. The gradually decreasing C content (calculated after 60 seconds Ar^+ etching) in our case from 82% to 20% and 62% to 21% with increasing T_s from RT to 350°C at constant RF power of 40 W and 50 W respectively (shown in Fig. 1) must be due to enhanced desorption of the methane gas from the surface of the growing film at higher T_s [14,20]. As can be observed from Fig. 1, Ge3d atomic percentage increases as T_s is increased. On the other hand, maximum C1s concentration of 26.25% and 25.71% is observed at 40 W and 50 W respectively for the films deposited at 250°C . This suggests that lower RF power results in higher C atomic concentration in the films, which is consistent with previously published results [11, 22]. Hydrogen concentration in the films are found negligible from XPS data, so it is not included in the discussion.

Fig. 2 shows the full-range XPS scan for a- $\text{Ge}_x\text{C}_{1-x}$ film deposited at 250°C , 50 W before and after Ar^+ ion bombardment for 60 s, with three main peaks corresponding to Ge3d, C1s and O1s. It can be seen that the O1s peak almost disappears after the sample surface was cleaned by

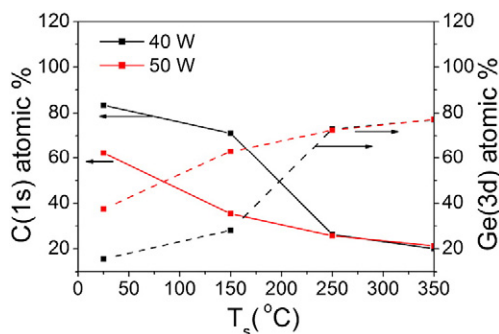


Fig. 1. Ge3d (dashed line) and C1s (solid line) atomic concentration with T_s at two different RF powers, 40 W (black) and 50 W (red).

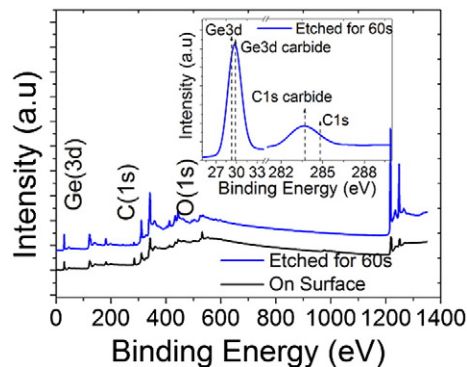


Fig. 2. XPS spectra of a- $\text{Ge}_x\text{C}_{1-x}$ film before (black) and after (blue) surface etching by Ar^+ ion bombardment at 250°C , 50 W. Inset shows the core level spectra of Ge3d and C1s after Ar^+ etching for 60 s.

argon ion bombardment for 60 s (etch rate = 0.42 nm/s). This may suggest that oxygen impurity is mainly introduced when the sample is exposed to air rather than during the film deposition process. Similar spectra were obtained for other films deposited at different RF powers and substrate temperatures (not shown here). The measured core level spectra of the film after 60 seconds Ar^+ etching is shown as an inset in Fig. 2. The peak position of C1s at $283.8 \text{ eV} \pm 0.02 \text{ eV}$, which is lower than the elemental C1s peak position of 284.8 eV [20,21], is the evidence to support a carbide formation. At the same time the shift of the peak position of elemental Ge3d (29.2 eV) [21] to a higher binding energy to $29.9 \text{ eV} \pm 0.01 \text{ eV}$ further substantiates that Ge is bonded to C [20]. This might be due to charge transfer caused by an electronegativity difference between carbon and germanium (Pauling electronegativities: ~ 2.01 for Ge and ~ 2.55 for carbon) [7,23]. In order to investigate further, XPS peak fitting analysis of C1s peaks at different temperatures and RF powers was conducted to characterize the composition and chemical bonding state in the films.

Fig. 3 shows fits to the C1s signals for the samples grown at various T_s and RF powers. Fig. 3a shows the results of XPS data analysis, where (a) is the XPS peak fitted C1s narrow scan on a- $\text{Ge}_x\text{C}_{1-x}$ films after argon ion bombardment for 60 s, (b) is the variation of binding energy (BE) of C—C, and Ge—C bonds and, (c) is the relative integrated intensity of C—C and Ge—C bonds as a function of T_s with two different RF powers. The C1s spectra of a- $\text{Ge}_x\text{C}_{1-x}$ films were fitted by using two Gaussian components using a Levenberg–Marquardt (L–M) peak analyser algorithm keeping peak centre and FWHM as free parameters. It is evident that the quality of the fit is very good with r-square (coefficient of determination) value close to 0.99. Variation of BE data of the Ge—C, and C—C in $\text{Ge}_x\text{C}_{1-x}$ films deposited at different T_s are shown in Fig. 3(b). A significant change can be observed in Fig. 3(b) as T_s changed from RT to 350°C . First, the C1s core level shifted when T_s changed from RT to 350°C , indicating that the chemical environment surrounding C atoms was significantly influenced by T_s . Second, asymmetry of the C1s curve became more severe with a tail appearing towards high energy with increasing T_s . The signals at $284.5 \pm 0.3 \text{ eV}$ are assigned to C—C sites while the modulation at lower energy ($283.5 \pm 0.3 \text{ eV}$) [24] is considered to be Ge—C. No C—C bond is found at $T_s = 250^\circ\text{C}$. It could be observed from Fig. 3(a) that no Ge—C bond is formed at RT as expected. The number of Ge—C bonds increases with increasing T_s but tends to decrease beyond $T_s = 250^\circ\text{C}$, accompanied by a change in the fraction of C—C bonds. From the relative integrated intensity of the three components as shown in Fig. 3(c), it could be observed that the fraction of Ge—C bonds increases with increasing T_s and tends to decrease for $T_s > 250^\circ\text{C}$, accompanied by an increase in the fraction of C—C bonds.

The uncertainty in the peak positions is $\pm 0.1 \text{ eV}$, FWHM $\pm 0.1 \text{ eV}$, and the relative areas $\pm 5\%$.

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