Thin Solid Films 592 (2015) 162–166

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Synthesis of nano-crystalline germanium carbide using radio frequency magnetron sputtering

Neeti Gupta *, Binesh Puthen Veettil, Hongze Xia, Siva Krishna Karuturi, Gavin Conibeer, Santosh Shrestha

School of Photovoltaic and Renewable Energy Engineering, UNSW, Sydney, NSW 2052, Australia

ARTICLE INFO

Article history:
Received 16 October 2014
Received in revised form 4 September 2015
Accepted 8 September 2015
Available online 10 September 2015

Keywords:
Nano-crystalline
Germanium carbide
Sputtering
Absorber
X-ray photoelectron spectroscopy
Transmission electron microscopy

ABSTRACT

Nano-crystalline Ge_xC_{1-x} is a potential third generation solar cell absorber material due to its favourable optoelectronic properties and relatively high abundance of elements. The ability to grow nano-crystalline Ge_xC_{1-x} in large areas by an industry-friendly process can enhance its scope as a photovoltaic absorber. In this work nano-crystalline Ge_xC_{1-x} thin films have been grown on Si (100) substrate using radio frequency magnetron sputtering. The crystallinity, composition, structure and optical properties of the films were determined by, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, atomic force microscopy, transmission electron microscopy (TEM) and ultra-violet visible infrared spectroscopy. From TEM results it was found that Ge_xC_{1-x} crystals were scattered in the film with d-spacing of 3.4 nm between the fringes (calculated a = 5.53 Å), but that a small number of nanoparticles of GeC were present. The Raman signature of the local Ge–C mode is identified near 530 cm^{-1} in Ge_xC_{1-x} film grown at 350 °C. The band gap energy value was estimated to be 0.90 eV from optical reflectance spectra. Maximum 15.5% of Ge_xC_{1-x} is found in the film deposited at 350 °C using XPS fitting.

1. Introduction

Germanium-based crystalline semiconductors have been studied in detail for their significant potential in optoelectronic applications such as optical detectors [1–7]. Although Ge_xC_{1-x} has been widely researched for its use in infrared windows [3,8–10] it has gained only a little attention in photovoltaic applications. Ge_xC_{1-x} can provide tunable band gap [11–13] and high absorption coefficient [14] and controllable photon energy as a photovoltaic absorber for third generation photovoltaic cells such as hot carrier solar cells [15] and tandem solar cells [16].

Ge_xC_{1-x} is an indirect band gap semiconducting material, which crystallises in both cubic (zinc blende) and hexagonal (wurtzite) phases [17]. Band gap tuning required for the tandem cell applications can be achieved by exploiting the quantum confinement properties of the size-controlled nano-crystalline Ge_xC_{1-x} [18]. Ge_xC_{1-x} is nontoxic and contains reasonably abundant elements. However, it is more complex to fabricate compared to SiC, mainly due to large lattice constant mismatch (37% between diamond (a_c = 3.5668 Å) and Ge (a_{Ge} = 5.668 Å)), thermodynamic instability and low solubility of carbon in Ge (1×10^8 cm^{-3} at the melting point of Ge) [19–21] at all temperatures and pressures. Epitaxial growth of $Ge_{1-x}C_x$ films on Si (001) with less than 1% carbon using molecular beam epitaxy has been reported by Osten et al. [1,2].

The growth of GeC has also been investigated using various fabrication methods such as molecular beam epitaxy [1,2], reactive sputtering [3–5,16,22,23], chemical vapour deposition [6], and activated reactive evaporation [7]. Li et al. [16] and Che et al. [23] have concluded that the co-sputtering fabrication process is more favourable to form Ge–C bonds than reactive sputtering and studied structural and optical properties of amorphous $Ge_{1-x}C_x$ films. However, fabrication of nano-crystalline Ge_xC_{1-x} (nc-Ge_xC_{1-x}) using RF magnetron co-sputtering has not been reported. The advantage of sputtering over other fabrication methods includes simplicity, potential for high throughput and better uniformity over a large area.

2. Materials and methods

In this work, the Ge_xC_{1-x} films have been grown on Si (100) and quartz substrates using a home-built radio frequency magnetron sputtering system. The base pressure was lower than 5×10^{-4} Pa. Silicon and quartz substrates were chemically cleaned using piranha solution and silicon substrates were dipped in 4% hydrofluoric acid to remove oxide from its surface prior to loading into the sputter chamber. The films were deposited at various temperatures with 50 W RF power for an hour. The sputter target (Ge strips on a graphite target) was pre-sputtered using argon gas before deposition for, at least, 10 min to remove surface oxides and other impurities. The coverage area of Ge on the graphite target was approximately 40%.

* Corresponding author.
E-mail addresses: neeti.gupta@student.unsw.edu.au, neeti.gupta30@gmail.com (N. Gupta).

http://dx.doi.org/10.1016/j.tsf.2015.09.014
0040-6090/

Chemical composition of the films was determined by ESCALAB250Xi X-ray photoelectron spectroscopy (XPS) using mono-chromatic Al Kα (λ = 1486.68 eV) X-ray source with a power of 164 W (10.8 mA and 15.2 kV). The electron energy analyser was set at 100 eV pass energy for survey scans and 50 eV for depth profiling

region scans. During depth profile Ar ion beam of 3 keV has been used to etch a square area of 2.5 mm × 2.5 mm with reference etching rate of 0.42 nm/s for Ta_2O_5. C1 s = 285.0 eV adventitious hydrocarbon was used as binding energy reference. XPS peak fit analysis has been performed with three Gaussian components using a Levenberg–Marquardt (L–M) peak analyser algorithm keeping peak centre and full width half maximum as free parameters. The Ge_xC_{1-x} quantum dots were observed by transmission electron microscope (TEM) using Philips CM200 and CM300. The TEM specimen was prepared by ion-beam milling and the small angle cleavage technique for the cross-sectional and plan-view observations, respectively. The specimen thickness was less than 100 nm for the cross-section imaging and less than 50 nm for plan view imaging.

Raman measurements were performed using a Renishaw in-Via Raman microscopes using the 514 nm line of an Ar^+ laser with spectral resolution of 1–2 cm^{-1}. Transmission spectra and optical reflection were measured by UV–Vis-NIR (Perkin-Elmer Lambda 1050) spectro-photometer attached to universal reflectance accessory (URA). Film deposited on quartz substrate was used to measure the transmittance and reflectance measurement as it does not absorb light itself in the visible, near infrared and ultra violet ranges.

3. Results and discussion

In order to characterize the deposition uniformity and surface roughness of the as-deposited films, atomic force microscopy (AFM) measurements were carried out using a Bruker Dimension ICON. Fig. 1 shows an AFM image of the film deposited at 350 °C with 50 W RF power on a Si (100) substrate. The film has a root mean square (RMS) roughness of about 4 nm, indicating uniform deposition with low surface roughness.

Fig. 2 shows high resolution TEM of the sample deposited at 350 °C. The TEM image shows that the film is polycrystalline in nature with germanium carbide nano-crystals scattered in the film. From the TEM image, we calculated d-spacing which is around 3.4 nm that gives a lattice constant of 5.53 Å. This is consistent with the value published by M. Todd and J. Kouvetakis (lattice constant GeC = 5.54 Å) [24]. An amorphous SiO_2 layer of about 2.2 nm is speculated between Si

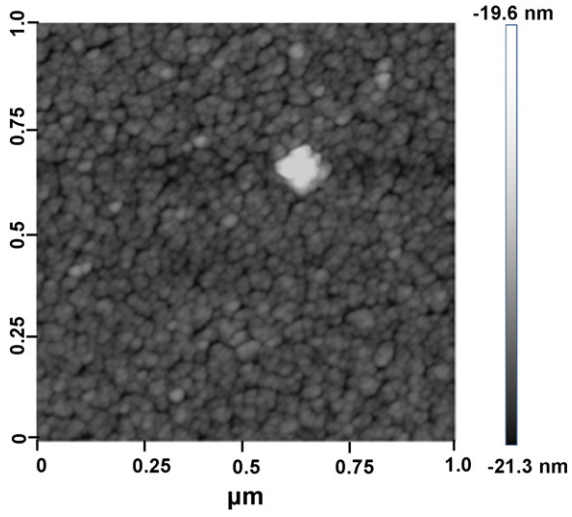

Fig. 1. AFM image of a Ge_xC_{1-x} film deposited at 350 °C with 50 W RF power on a Si (100) substrate. The surface roughness is about 4 nm.

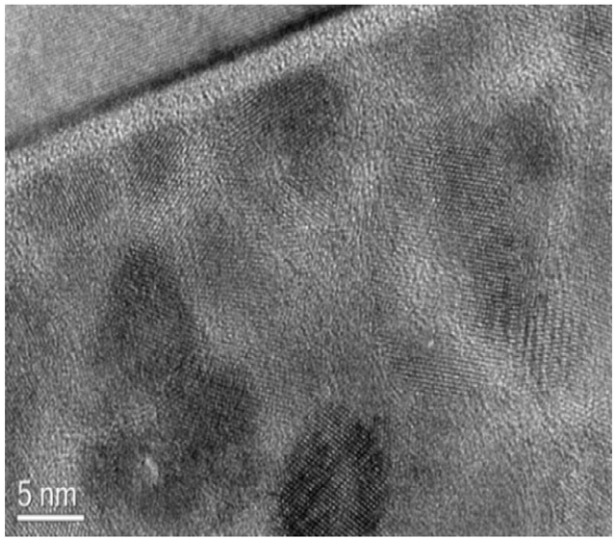

Fig. 2. HRTEM image showing poly-crystalline growth of Ge_xC_{1-x} on Si. The film was deposited at 350 °C.

substrate and the Ge_xC_{1-x} film. This might be because of oxidation of the substrate in the deposition chamber.

The structural properties of the crystal were analysed using a numerical model. In this model, we assumed a unit cell of 4 atoms, i.e., 1 C and 3 Ge, arranged in a zinc blende like crystal structure. With the help of Quantum Espresso [25], self-consistent-field calculations were performed on the postulated system within the framework of Density Functional Theorem. Two norm-conserving Perdew–Burke–

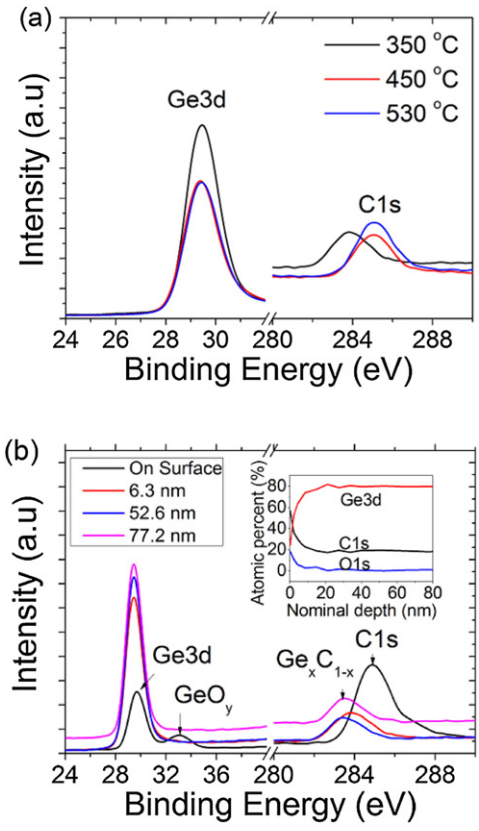

Fig. 3. (a): Ge3d and C1s XPS spectra of a film Ge_xC_{1-x} grown on Si (100) at different substrate temperature with R_f = 50 W.(b) Ge3d and C1s XPS spectra of Ge_xC_{1-x} grown on Si (100) at 350 °C with R_f = 50 W at different depths. Inset shows atomic composition of C1s, Ge3d and O1s with nominal depth (nm).