Formation of Uniform Germanium Islands on Silicon Substrate Using Nickel as Catalyst by Thermal Evaporation Method

M. M. JUMIDALI[a,b,c,*], M. R. HASHIM[a], A. ABDUL AZIZ[a], A. F. ABD RAHIM[a,d]

[a]Nano-Optoelectronics Research Laboratory, School of Physics,
Universiti Sains Malaysia 11800, Pulau-Pinang, Malaysia

[b]Faculty of Applied Sciences, Universiti Teknologi MARA Malaysia, 40450 Malaysia

[c]Department of Applied Sciences, Universiti Teknologi
MARA Pulau Pinang, 13500 Pulau Pinang, Malaysia

[d]Faculty of Electrical Engineering, Universiti Teknologi
MARA Pulau Pinang, 13500 Pulau Pinang, Malaysia

Uniform germanium islands (GIs) were grown on Si (100) using a nickel layer as catalyst through the physical vapor deposition of germanium (Ge) powder at 1000 °C at different deposition times. Prior to the deposition of Ge layer, nickel (Ni) catalyst was deposited on silicon substrates via radio frequency magnetron sputtering technique. Scanning electron microscopy results showed that the increase in deposition time resulted in a variation in surface morphology. Energy dispersive X-ray spectrometer analysis found that the GI samples composed of Ni element indicating the role of Ni in uniform Ge islands formation. The X-ray diffraction pattern spectra revealed that the GIs exhibited a Ge cubic structure and the intensity of Ge peaks varies with deposition time. In-plane strain indicated that the strain caused by the substrate is tensile and changed to compressive strain at the longer deposition time. The Raman spectra exhibited a red shift in the Ge–Ge peak, compared with the bulk Ge, as a result of compressive strain of the GIs. Fourier transform infrared spectrum analysis also indicated that the optical band gap *Eg* values of GIs can be varied by deposition time.

1. Introduction

The formation mechanisms and properties of germanium islands (GIs) on Si structures are of great interest for use in new optoelectronic devices. Several methods are employed to fabricate GIs with different sizes, such as chemical vapor deposition [1, 2], radio frequency magnetron sputtering [3, 4], molecular beam epitaxy [5–7], and thermal evaporation [8]. However, establishing a method to achieve sufficiently uniform island sizes with regular spatial distribution remains a critical issue. Substantial research focused on the size distribution of the islands because such islands are an important aspect in practical application [9]. The conventional way to control island formation (size, shape and density) is to vary growth conditions by altering substrate temperature and molecular flux [9].

Metals modify nucleation and growth phenomena normally used to tune the characteristics of epitaxial islands. Nickel (Ni) is a material that has promising use as a metal catalyst. For instance, Tuan *et al.* [10] and Hsu *et al.* [11] successfully synthesized Ge and Si nanowires using Ni

catalysts. Recently, Kolahdouz *et al.* [12] used Ni as a metal catalyst to form islands based on substrate engineering to control the diameter of carbon multi-walled nano-tubes. The use of Ni as a catalyst for GI growth via thermal evaporation is very promising because, thermodynamically, Ni is easy to agglomerate with Ge. The Ni/Ge alloy has a low eutectic temperature at 762 °C. This character allows the easy formation of Ni/Ge alloy liquid droplets on a Si substrate and serves as a trap of growth species for GI formation. In this paper, we report on a fabrication of GI on an n-Si substrate grown via simple thermal evaporation method using a Ni epitaxial layer as catalyst. The roles of Ni in GI formation on Si (100) necessitate further study because no such report is available in the literature. Significant different GI behaviors are observed when deposition time varies. The structural and optical properties of the formed islands are characterized and investigated.

2. Experimental procedures

The germanium islands (GIs) were synthesized in a horizontal tube furnace system by the simple thermal evaporation method in the presence of nickel (Ni) metal layer on the silicon (Si) substrate as the catalyst. The Ni-coated Si substrates (thickness ∼250 nm) were prepared by A500 Edwards RF magnetron sputtering system. The Ni-coated substrates were placed upside down

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*corresponding author; e-mail:
mohdmuza433@ppinang.uitm.edu.my

on top of the alumina boat to act as substrate for GIs growth. The 99.999% of Ge powder act as starting materials were then heated up to 1000 °C under a Nitrogen (N_2) atmosphere for different hours. To study the heating time effect, the samples were heated to a particular time in a flow of N_2 gas. After deposition process, the samples were drawn out and cooled to room temperature for analysis. The as-grown products were structurally characterized by a X-ray diffractometer (PAN analytical X'Pert PRO diffractometer with Cu-K_α radiation). Scanning electron microscopy (JEOL JSM-6460LV with energy dispersive X-ray spectroscopy, EDX) was used to analyze the morphology of the products. Room temperature Raman spectrum was taken with a Raman spectrometer (Horiba Jobin Yvon HR800), with Ar+ as excition source operating at a wavelength of 514.55 nm. The FTIR spectra were collected by a Perkin Elmer Fourier Transform Infrared Spectrometer for characterizing the optical properties of GIs.

3. Results and discussion

Figure 1a to 1d show the scanning electron microscopy (SEM) images of synthesized GIs on a Ni-coated Si substrate for different growth times (from 1 h to 3 h). The images revealed that different GI shapes are distributed randomly on the Si surface as the deposition time increases. Figure 1a show the images of sample growth for 1 h, which consists of small- and medium-sized sphere GIs. All the islands were grown randomly, and some of a Ni cluster remained on the Si substrate. As the growth time increased to 2 h, GI morphology on the Si substrate changed to the bigger size of spherical shaped GIs without any remaining Ni cluster on the Si substrate (Fig. 1b). The increase on size of GIs affirmed that the GIs were coarsening (i.e., the movement of nucleated GIs from smaller to larger islands results in increased GI size). Increasing the heating time to 3 h (Fig. 1c) resulted in the formation of irregular shape of GIs on the substrate. Higher magnification image (Fig. 1d) confirmed that the irregular shape of GIs due to formation of SiO_2 around the islands (the samples have mushroom-like feature). Energy-dispersive X-ray spectroscopy (EDX) analysis was performed on the particular islands to study the distribution of material compounds on the island. The EDX images shown in the inset of Fig. 1a, 1b and 1c indicate that all the GIs consisted primarily of Ge and Ni elements, as well as small amounts of Si and O elements in sample 1 and 2 hour. Sample for 3 hour shows the highest Si and O elements suggested the GIs were contaminated by SiO_2. Ni content was clearly preserved as the deposition time increased, which also shows the role of Ni in GIs formation.

Figures 2a to 2c illustrate the XRD patterns of the GI film prepared at different heating times for 1, 2, and 3 h, respectively. The diffraction peaks observed in the produced GIs film mainly corresponds to a cubic-type Ge structure with preferred orientations at the (111),
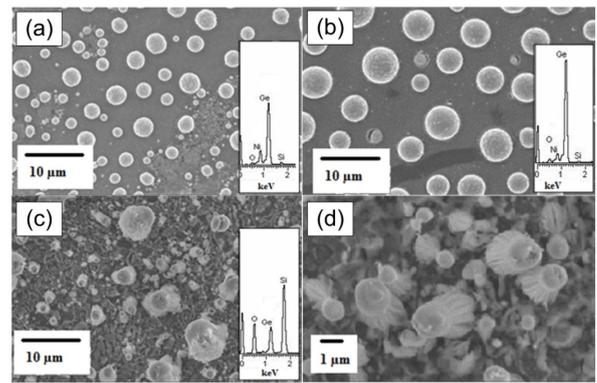
Fig. 1. The SEM images and inset EDX spectra of GIs grown on Si substrate for (a) 1 hour, (b) 2 hours, (c) 3 hours deposition times respectively and (d) high magnification of SEM image of 3 hours deposition time.

(220), and (311) planes. The intensity of the Ge peaks increase as deposition time increase from one to two hours deposition time and rapidly decreased at longer deposition times (3 hour). The decrease of the Ge intensity peaks suggested that the GIs were covered by SiO_2. The nanometer-scale amorphous Si was reported to be vaporized above 1000 °C [13]. Therefore, at the longer heating times the amorphous Si vapor from Si substrate will possibly diffuse in GIs structures and with easily presence of oxygen at high temperature will allow the formation of SiO_2. The existence of the Ni/Ge alloy on each sample shows the role of Ni in the formation of GI structures. Table I summarizes the full width at half
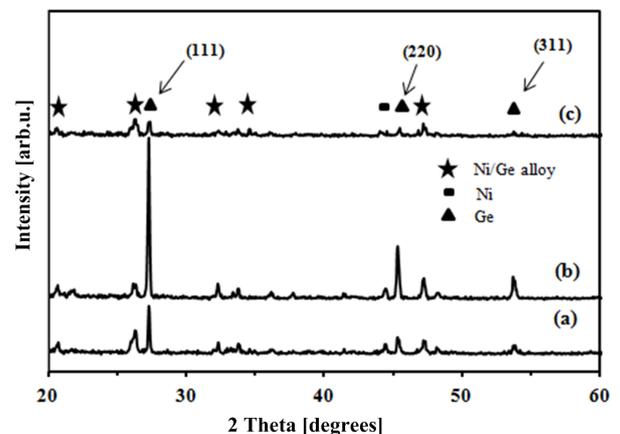
Fig. 2. XRD patterns of the GI film prepared at different heating times for (a) 1, (b) 2, and (c) 3 hours, respectively.

maximum (FWHM) of the (111) plane, crystallite size (D_P), lattice constant, and strain for the GI films prepared at different deposition times. With an increase in deposition time, the FWHM becomes narrower; hence, the crystallite size increases. The increasing crystallite size can be due to the increasing number of Ge particles

collected during the longer deposition time. The lattice constant results also shown increases suggested that the unit cell is elongated along the axis and the compressive forces act in the plane of the film. The lattice constant can be further utilized to evaluate the average uniform strain in the lattice along the a-axis. The positive value of the in-plane strain ε_a for the 1 hour and two hour deposition times indicates that the strain caused by the substrate is tensile. The tensile strain values increased when heating time was increased are in good agreement with the results reported by Hartmann *et al.* [14]. The negative value of the in-plane strain ε_a for the longer deposition time (3 hour) shows that the strain caused by the substrate is compressive. Figure 3 shows the Raman

XRD data of GIs growth   TABLE I

Deposition Time [Hour]	2θ	FWHM [nm]	D_P [nm]	Lattice constant a [Å]	Strain (ε_a) $\times 10^{-3}$
1	27.2851	0.2952	27.69	5.66133	+0.234982
2	27.2735	0.1968	41.54	5.66370	+0.653710
3	27.3025	0.1968	41.54	5.65783	−0.383392

spectra of the three samples grown on Si at different deposition times. With increased deposition time, the samples show a decrease in peak intensity and an increase in FWHM, demonstrating that the quality of the GIs is reduced when heating time is increased.

The peaks around 300 cm^{-1} are attributed to the optical phonon contribution of the Ge-Ge stretching mode [15]. The red-shifted trend for sample grown compared to that of the bulk Ge (300 cm^{-1}) [16] is compatible with the previous XRD result, which suggests that the sample experienced tensile strain for 1 and 2 hour deposition and compressive strain for 3 hour heating times. Another low and broad hump peak centered at about 446.0 cm^{-1}. There are no reports of the Raman peak for Ni-Ge alloys in the literature and according to our XRD spectra, the peak at 446.0 cm^{-1} is suggested attribute to the Ni-Ge phase. The absence of Si/Ge vibration peaks about 400 cm^{-1} corresponds to the Si/Ge alloy mode [17] implies there is no intermixing of Si from the substrate with GIs. The higher peak at 520 cm^{-1} is attributed to the optical phonon mode of the Si substrate [18]. The optical band gap (Eg) for GI films were determined by analyzing the optical data, with the expression of the optical absorbance α and the incident photon energy $h\nu$, using the Tauc equation [19]. The band gaps were determined by plotting $(\alpha\,h\nu)^{3/2}$ versus $h\nu$ (Fig. 4). The optical results (Fig. 4) have shown that Eg was found to decrease as heating time increased. This finding is in good agreement with the results reported [20]. The lower values of the energy band gap are attributable to the well known close relationship between the band gap and crystallites size. In another related observation, the Eg red shift can be due to an increase in crystal intrinsic defects as a result of impurities that come from the formation of SiO_2 in the GIs structure due to longer heating time.
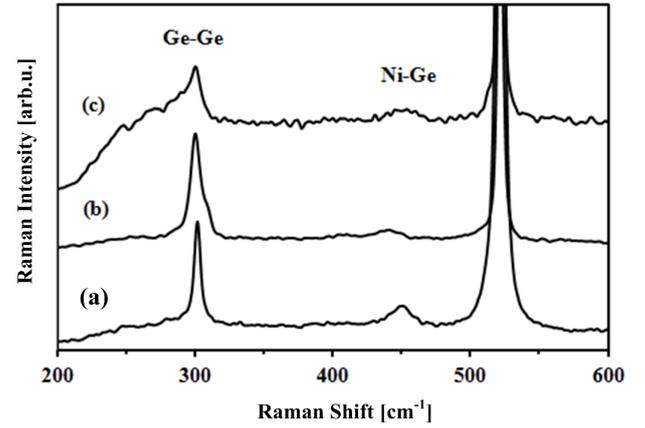
Fig. 3. Raman spectra of the GI film prepared at different heating times for (a) 1, (b) 2, and (c) 3 hours, respectively.
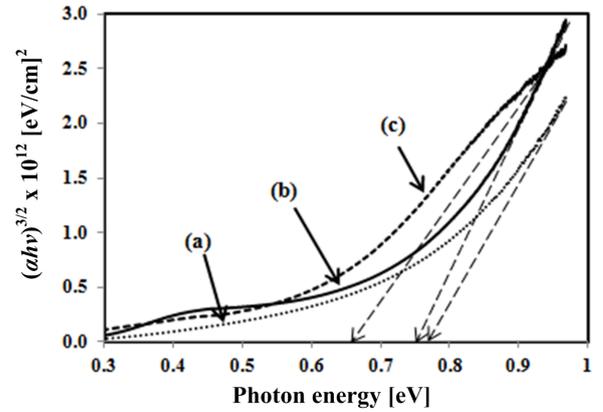
Fig. 4. $(\alpha\,h\nu)^{3/2}$ vs $h\nu$ plot of GIs with different deposition time: (a) 1 h, (b) 2 h, and (c) 3 hours.

4. Conclusions

In summary, the morphological, structural, and optical properties of GIs synthesized through simple thermal evaporation using a Ni catalyst were investigated. SEM images showed that the morphology of GI structures changes with different deposition times. The XRD measurements revealed that GIs have good crystal quality of crystalline Ge cubic phase and a small amount of crystalline Ni/Ge alloy. Room-temperature Raman scattering indicated that the samples were in the Ge–Ge stretching mode and red-shifted as the longer deposition time. The energy band gap decreased as the deposition time increased because of the increase in particle size in the GIs.

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