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Room temperature photoluminescence and dc resistivity of $Si_{0.95}Ge_{0.05}$ alloy nanowires grown in microwave H-field

Charu Lata Dube[a], Subhash C. Kashyap[a,*], D.C. Dube[b], D.K. Agarwal[c]

[a] Department of Physics, Indian Institute of Technology Delhi, Hauz Khas, N. Delhi 110016, India
[b] Electronics and Communication Department, Institute of Technology and Management, Gurgaon, Haryana 122017, India
[c] Materials Research Institute, The Pennsylvania State Univ., University Park, PA 16802, USA

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ABSTRACT

In the present work, $Si_{0.95}Ge_{0.05}$ alloy nanowires were synthesised in a single-mode resonant cavity operated in H_{011} mode in ambient at 2.45 GHz in a short duration (5 min) and at a temperature (900 °C) lower than the equilibrium alloy-phase formation temperature. The photoluminescence (PL) studies were carried out at room temperature. The intense PL peaks, in the energy range of 2.9–3.6 eV, can be ascribed to radiative recombination of the generated carriers. The low temperature (100–250 K) dc electrical-transport is investigated; and the activation energy is estimated to be lower by an order than that of polycrystalline samples. The lower activation energy is possibly due to electronic/structural defects introduced by the non-equilibrium growth process and high aspect ratio of the grown nanostructure. With these improved characteristics, the alloy nanowires can be exploited for device fabrication.

1. Introduction

Silicon is a well established material in semiconductor industry. Alloying of silicon with germanium widens the scope of its applications for several electronic and optoelectronic devices including thermo-generators, photo detectors, X-ray- and neutron-monochromators, solar cells, and as a lattice-matched substrate for silicon–germanium (SiGe) epitaxial growth, etc. [1,2]. The light emission efficiency of silicon can be improved by lifting up the lattice periodicity and thereby inducing an uncertainty in the *k*-space. Various attempts have been made to disrupt lattice periodicity, thus allowing no-phonon assisted optical transition which enhances light-emitting properties of silicon, for e.g. alloying of silicon with germanium [3], synthesis of silicon nanostructures [4] and growth of Si/SiO_x structures [5], etc. Nanowires of different materials are grown by vapour–liquid–solid (VLS) method [6], laser ablation [7], physical thermal evaporation [4], molecular beam epitaxy [8], solution growth [9], multimode microwave (MW) processing [10], and more recently by single-mode MW processing [11]. The microwave processing has many advantages over existing growth techniques, including faster processing, nearly uniform volumetric heating, rapid alloy formation, and de-crystallization/new phase formation [12–14]. There are reports describing the application of multimode MW cavities [15] and of a single-mode cavity [16,17] for the processing of different materials.

In the present work, therefore, $Si_{0.95}Ge_{0.05}$ alloy nanowires, synthesised at a low MW power of ~300 W in a single-mode resonant cavity are characterized for their structural, optical and electrical-transport properties to explore their suitability for various optoelectronic devices.

2. Experimental

The schematic of experimental set-up for single-mode MW processing of the sample is given elsewhere [11]. It comprises of magnetron, circulator, applicator (cylindrical resonant cavity to sustain H_{011} mode) and associated hardware for impedance matching. Appropriate quantities of silicon and germanium powders, required for making $Si_{0.95}Ge_{0.05}$ alloy, were thoroughly mixed in a ball milling machine for 24 h; and the resulting mixture was then pelletized. The pellet of $Si_{0.95}Ge_{0.05}$ mixture was put at the centre of the cylindrical resonant cavity and processed in the ambient atmosphere.

The processing temperature of the sample was maintained for a stipulated period (2–5 min) by monitoring the power fed to the cavity. The pellets of the starting mixture (labeled as 5SG) were MW processed in different runs at 800 °C for 2 min, 900 °C for 2 min and 900 °C for 5 min. The processed pellets were labeled as 5SG1, 5SG2, 5SG3, respectively.

The phase analysis of the starting mixture and of MW processed pellets was carried out by employing X-ray diffractometer (Philips X'Pert PRO). The scanning electron micrograph (SEM) is recorded by employing Electron Microscope Zeiss EVO 50. The photoluminescence (PL) properties of synthesised nanowires were studied at room temperature using spectrofluorometer (Fluorolog FL3-11) in the spectral range of 2.9–3.6 eV with excitation energy of 3.8 eV. The detector type of spectrofluorometer is photo-multiplier tube. The resistance vs. temperature (*R*–*T*) data was taken using four probe contact method (CIP mode), ensuring ohmic contacts.

* Corresponding author. Fax: +91 11 26581114.
E-mail address: skashyap62@yahoo.com (S.C. Kashyap).

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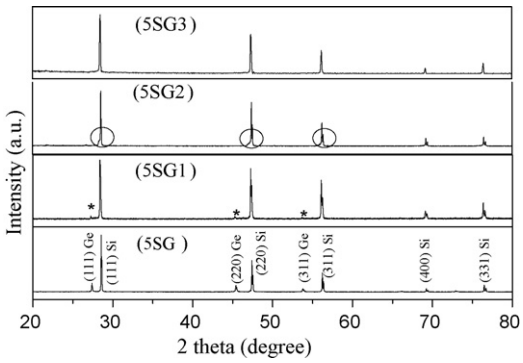

Fig. 1. The X-ray diffractogram of starting mixture and microwave processed pellets.

3. Results and discussion

Figure 1 shows X-ray diffractograms (XRD) of the 5SG, 5SG1, 5SG2 and 5SG3 samples. The XRD peaks have been identified by the second derivative method, and fitted by pseudo-Voigt functions. The XRD of starting mixture (sample 5SG) understandably shows the prominent reflections corresponding to both the constituents—Si and Ge, and of the processed pellets establishes the alloy formation. The increase in the values of lattice parameter "*a*", estimated for different samples, follows Vegard's law and thus establishes the germanium incorporation in the silicon lattice, which increases with the increase in processing temperature as well as processing time.

A few low intensity peaks in the XRD scan of the 5SG1 marked with '*' correspond to residual Ge in the sample. The shape of the peak in the XRD scan of the 5SG2, processed at 900 °C (highlighted in the encircled area) does not fit to Gaussian function, which in turn indicates that MW synthesised alloy may not be a single phase. It may be noticed from the XRD of the sample 5SG3, prepared at processing temperature of 900 °C and MW exposure time of 5 min, that there are no peaks corresponding to elemental Ge, and that the shape of the XRD peaks (corresponding to SiGe alloy) fits well to the Gaussian function. Therefore, the processing temperature of 900 °C and MW exposure time of 5 min are adequate for complete incorporation of Ge in the Si lattice i.e. alloying. Since the processing is being carried out in ambient and at 900 °C, surface oxidation of the nanowires cannot be ruled out.

The SEM of sample 5SG3, as shown in Fig. 2, reveals the formation of nanowires as well as nanostructures. The SEM image obtained at higher resolution (shown in inset of Fig. 2) shows that $Si_{0.95}Ge_{0.05}$ alloy nanowires are randomly entangled, and are quite long (>1 μm) of nearly 100 nm in diameter. The elemental composition of nanowires is determined by energy dispersive analysis of X-rays (EDAX). The EDAX spectrum of the sample (5SG3), as shown in the inset of Fig. 2, reveals that the nanowires are mainly comprised of silicon and germanium with small fraction of oxide and oxynitride on the surface of nanowires due to growth in the ambient.

The photoluminescence (PL) spectrum of MW synthesised nanowires, as shown in Fig. 3, shows strong emission peaks between 2.9 and 3.6 eV. The small dimension of nanowires (less than 100 nm) will encourage the generated free hot carriers to undergo ballistic transport [18]. Most of these carriers will reach the SiGe alloy and oxide/oxynitride interface, and will be trapped by the luminescent centres present at the interface. Nishikawa et al. [19] observed several luminescence bands with different peak energies ranging from 1.9 to 4.3 eV in porous silicon. As proposed by Nishikawa et al., the observed intensive blue light emission at 3.0 eV can be attributed to some intrinsic defect centres (present

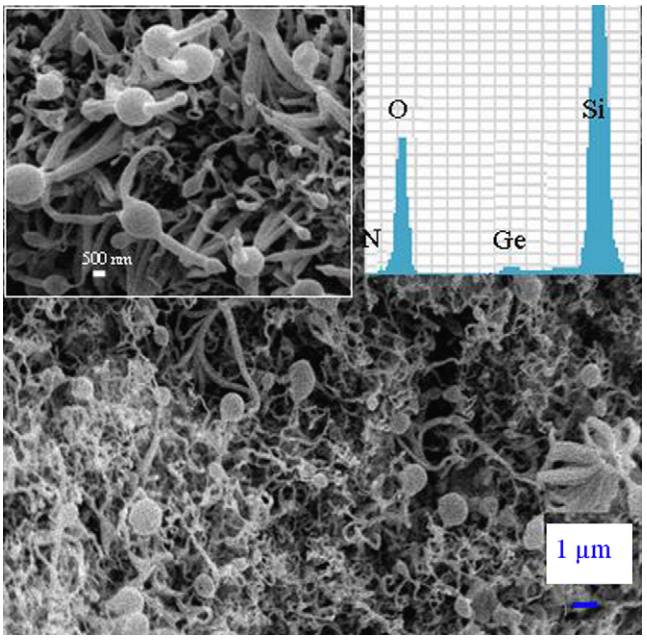

Fig. 2. SEM pictures of $Si_{0.95}Ge_{0.05}$ alloy nanowire.

in oxide/oxynitride sheath covering the alloy nanowires), which act as radiative recombination centres. Further, Qin et al. have also observed the blue light emission at 3.4 and 3.5 eV and explained on the basis of quantum confinement luminescence model [20]. Therefore, the blue light emission at 3.4 and 3.5 eV is ascribed to recombination at luminescent centre (having light-emitting energies in blue region) at the interface of the alloy and sheath.

The resistivity of the sample 5SG3 is calculated from the experimental data; and its variation with temperature ($\ln(\rho)$ vs. $T^{-1/4}$) from 100 to 250 K is shown in Fig. 4. The nature of contacts between the sample and metal (Ag) (in the scanned range of temperature) is established to be ohmic by the observed linearity of current–voltage (*I–V*) curve as shown in the inset of Fig. 4. The density of dangling bonds is known to be very high at grain boundaries in a polycrystalline material [21], and leads to the formation of trapping states. It is reported [22] that charge conduction at low temperature is due to hopping of charge carriers among trap states at the grain boundaries, and the variation of electrical resistivity with temperature follows Mott's relation. Since the diameter of the $Si_{0.95}Ge_{0.05}$ alloy nanowires (100 nm) is smaller than the Debye

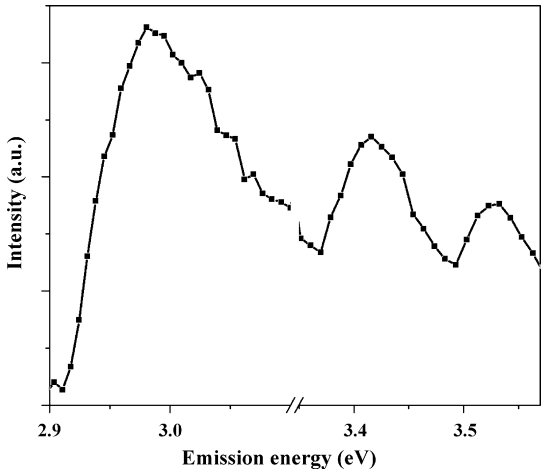

Fig. 3. Photoluminescence spectra from $Si_{0.95}Ge_{0.05}$ alloy nanowire.

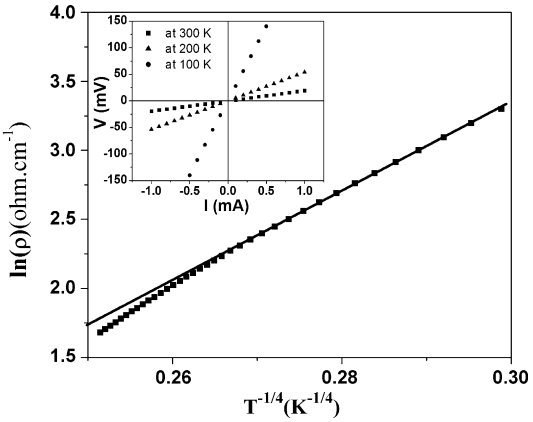

Fig. 4. Resistivity vs. temperature ($\ln(\rho)$ vs. $T^{-1/4}$) plot for $Si_{0.95}Ge_{0.05}$ alloy nanowire.

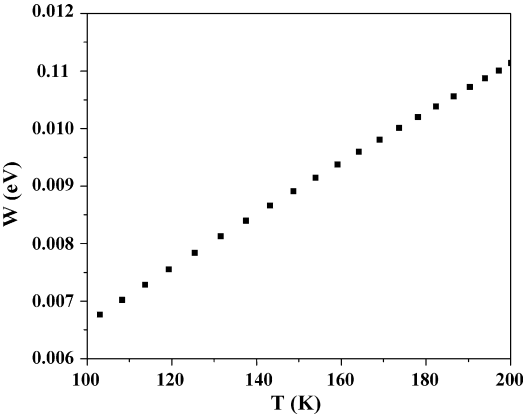

Fig. 5. The variation of Mott's parameter (W) with temperature for the $Si_{0.95}Ge_{0.05}$ alloy (nanowires).

length [23], and hence the core of the nanowires will be depleted of charge carriers, which indicates that possibly the charge transport is due to Variable Range Hopping (VRH) mechanism.

In the present case a good linear fit of Mott's relation [24] (between 100 and 200 K) reveals that current transport in the present case is due to hopping of carriers among trap states at the grain boundaries in the temperature regime of 100–200 K. It is, however, reported that [25], even if Mott's equation is satisfied, the charge transport can be different from VRH mechanism. Therefore, by employing a classical percolation theory, Mott's parameter, $W = k_B(T_0T^3)^{1/4}$, is calculated from the slope (T_0) of R vs. $T^{-1/4}$ plot [26], and its variation with temperature is shown in Fig. 5. The decrease in Mott's parameter (W) with the decrease in temperature, from 200 to 100 K, of 5SG3 confirms that the VRH mechanism of charge transport is operative in this temperature range. It is noteworthy that the estimated value of W is smaller (by an order) than the reported values for polycrystalline silicon [27]. The non-equilibrium growth of alloy nanowires along with high aspect ratio may be responsible for smaller value of activation energy. Nanostructures/nanowires have higher aspect ratio as compared to polycrystalline samples and, therefore, have increased defects/density of trap states. At low temperature, these present trap states will assist carrier transport [28] and thereby result in lower activation energy for synthesised nanostructures. It may be noted that at higher temperature the plot between $\ln(\rho)$ vs. $T^{-1/4}$ is no longer linear in nature. This behaviour can be attributed to changed carrier transport nature (most probably tunnelling) at higher temperatures (>200 K).

$Si_{0.95}Ge_{0.05}$ alloy nanowires are synthesised in a pure H-field operating at 2.45 GHz within 5 min at 900 °C. The alloy nanowires are efficient blue light emitters. It is proposed that both, the size-effect (diameter of nanowires ~100 nm) and the presence of luminescent centres in the oxide sheath of the nanowires are responsible for the efficient emission. The electron transport in the low temperature region (100–200 K) follows VRH mechanism with significantly low activation energy. The separated H-field MW processing, a green technique, has thus been successfully employed to synthesise $Si_{0.95}Ge_{0.05}$ nanowires in a short duration and at a lower temperature with improved device properties as blue light emitters.

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