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Structural and electrical analysis of poly-Ge films fabricated by e-beam evaporation for optoelectronic applications

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ABSTRACT

We have investigated the relationship between structural and electrical properties of Ge thin films deposited on single crystal silicon (100) substrates by electron beam evaporation at room temperature. Post-thermal annealing was applied to obtain poly-crystalline Ge thin films. The structural effects of the annealing temperature and annealing time on the crystallization of Ge films were analyzed using Raman and X-ray diffraction measurements. Raman and X-ray diffraction spectra revealed a structural evolution from amorphous to crystalline phase with increasing annealing temperature and annealing time. It was found that high quality poly-crystalline Ge films were obtained with crystallization ratio of 90% at an annealing temperarure of 500 °C following the crystallization threshold of 450 °C. Effects of structural ordering on the electrical properties were investigated through current-voltage characteristics of fabricated heterostructure devices (Ge/p-Si). Smooth cathode-anode interchange in the diode behavior has been clearly observed following the structural ordering as a function of annealing temperature in a systematic way. These outcomes could be exploited for engineering of low-cost Ge based novel electronic and opto-electronic devices.

1. Introduction

Although germanium (Ge) was the frontier material of early years of transistor and integrated circuit developments, it was later completely overruled by silicon (Si). After a long stagnancy, recently Ge has regained a lot of attention in the semiconductor industry due to its attractive electrical and optical properties. Ge has been used in several applications, such as high mobility transistors due to its higher electron and hole mobility [1,2] and high efficiency multijunction solar cells as a base material due to better absorption in infrared regime of the spectrum [3–5]. In spite of its possible applications, Ge could not be widely used in single crystalline wafer form because of the higher price compared to Si substrates. Therefore to take advantage of the superior properties of Ge, heterogeneous integration of high quality Ge thin film on Si platform is very crucial as well as taking advantage of very low temperature processing of Ge with respect to Si. Having its inherent electrical and optical superiorities, Ge thin films can be used in thin film transistor applications instead of Si [6]. Moreover, Ge thin films have small band gap of 0.67 eV resulting in better absorption in infrared regime of the spectrum, which makes Ge as an appropriate bottom junction for large scale thin film tandem solar cells and efficient photodetectors for telecom applications [7]. Recently several crystallization processes for amorphous Ge (α-Ge) have been widely investigated to obtain high quality poly-crystalline Ge (poly-Ge) thin films at low temperature, such as solid phase crystallization (SPC) [8], laser annealing [9] and metal-induced crystallization (MIC) [10,11]. Laser annealing requires high temperature and expensive processing. MIC is a low temperature processing but in this methods semiconductor properties are deteriorated due to metal contamination [12]. Therefore, SPC technique has been considered viable and widely used method to obtain high quality poly-Ge thin films at relatively low temperatures [8,13–15]. As expected, the crystallization is limited by the mobility of the Ge atoms. When α-Ge films are annealed to a certain temperature, Ge atoms reorganize themselves from an amorphous phase into a crystalline phase. Many studies have investigated structural and optical properties of crystallized germanium thin films. However, the relationship between the structural properties of Ge thin films and electrical properties of heterostructure devices fabricated

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using crystallized Ge thin films has not been investigated as a function of post annealing temperatures in a systematic way.

We have investigated and compared the structural and electrical properties of poly-Ge films deposited on c-Si (100) substrates by electron beam (e-beam) evaporation. Structural properties of Ge films were examined by Raman spectroscopy and X-ray diffraction (XRD) measurements. We have analyzed the influence of post-annealing temperatures and annealing time on the crystallinity and crystal orientation of Ge thin films. Current-voltage (I-V) results of the fabricated heterostructure devices were systematically discussed by considering structural characteristics of Ge films.

2. Experimental details

Amorphous Ge films were deposited on single crystalline p-Si (c-Si) (100) substrates by e-beam evaporation technique at room temperature. Prior to Ge deposition, the native silicon-oxide was removed from the substrate surface by chemical etching with diluted hydrofluoric acid (5%). Following substrate cleaning, Ge thin films were deposited by e-beam evaporation employing a 99.999% pure Ge. The deposition rate was set at 5.0 Å/s and the film thickness of α-Ge was about 300 nm. Ge thin films were investigated as a function of post annealing temperatures for 60 and 300 min at 300–500 °C in nitrogen (N_2) atmosphere for crystallization process.

Crystal quality and crystal orientations of the heat treated films were characterized by Raman spectra and X-ray diffraction (XRD) techniques, respectively. Raman spectra were measured using a Horiba-Jobin Yvon i550 system equipped with a CCD camera and a Nd: YAG laser with 532 nm wavelength as an excitation source. The crystal orientations of poly-Ge films were identified by a Rigaku MiniFlex X-ray diffractometer with monochromatic Cu-Kα incident beam (λ=0.154056 nm) in the θ–2θ scan geometry. Electrical properties of Ge films were determined by fabricating Ge/p-Si heterojunction devices. Ohmic contacts were formed by thermal evaporation of aluminium for I-V measurements. I-V characteristics of the devices were carried out to analyze the conductivity type and the measurements were done by Keithley 2440 source meter under no illumination. All measurements were carried out at room temperature.

3. Results and discussion

In order to evaluate the nucleation threshold and crystal quality of the deposited films with and without thermal annealing, Raman measurements were performed. Raman spectra of Ge films on c-Si (100) substrates after the SPC at 300–500 °C for 60 and 300 min are shown in Fig. 1(a) and Fig. 1(b), respectively. The spectra of as-deposited and c-Ge (single crystalline Ge wafer) are also shown for comparison. Independent of the annealing time all Raman spectrum of the samples annealed at a temperature lower than 450 °C gives broad Raman band with a peak position at around 276 cm^{-1} (see inset in Fig. 1(a) and in Fig. 1(b)). This broad (relatively less intense) peak indicates the amorphous nature of the film structures up to 400 °C annealing temperature. This peak could be addressed to local transverse optical (TO) phonons from random ordering of Ge atoms [16,17] and suggests that the crystallization threshold is higher than 400 °C. As the annealing temperature increased to 450 °C for 60 min, the onset of crystallization is reached, both amorphous and crystalline phase co-exist in the structure (Fig. 1(a)). The signal due to crystal phase at about 300 cm^{-1} is super-imposed to the signal of amorphous phase. With a further increase in annealing temperature, the spectrum become more symmetric and sharp reveals the almost complete transition from amorphous to poly-crystalline/crystalline form of the film structure at 500 °C. Increasing the annealing time from 60 to 300 min results in improvement in the crystal quality of the films, the intensity of the signal is much increased and almost reached to the signal intensity of reference Ge wafer (Fig. 1(b))..

In order to analyze the film structure and quality of the films that depend on annealing time, comparative peak positions and full-width at half maximum (FWHM) of the Ge thin films annealed at 300–500 °C for 60 and 300 min are given in Fig. 2. The peak position and FWHM of Ge wafer are also given for comparison. Up to 450 °C, the peak position of the films are about at 276 cm^{-1} and slightly blue shifted with the temperature in the Fig. 2(a). With the emergence of the crystalline phase (at 450 °C) where the peak position centered at 301 cm^{-1} blue shifted towards reference Ge signal and reaches 302 cm^{-1} with the maximum annealing temperature of 500 °C. The FWHM signal is one of the good indication of crystal quality of the films, the higher crystal quality gives the lower value of FWHM. As shown in the Fig. 2(b), the FWHM of the Raman signals is slowly decreasing with annealing temperature up to onset of crystallization which means that the amourphous structure of the film getting more homogeneous and regular compare to as deposited case. The FWHM value suddenly drops at the threshold temperature of 450 °C and gradually decreases and reaches 7 cm^{-1} at the maximum annealing temperature comparable to value of reference Ge (c-Ge wafer). For the pre-crystallization stage of annealing (annealing temperature is less than 450 °C) where the structure is in amorphous phase, the peak position of the Raman scattering spectrum is blue shifted accompanying remarkable shrinking in its FWHM with the prolonged annealing time from 60 to 300 min. This behavior suggest that, although film is in amorphous phase, the high degree of structural disorder tends to decrease with increase in annealing time and the local bonding configuration of Ge atoms are promoted to more regular form. Over the annealing temperature of 450 °C both peak position and FWHM values are slightly varying with increase in temperature and time of annealing. As seen in Fig. 2(a) and Fig. 2(b), the temperature is prominently effective in location and width of the Raman signal compare to time of annealing in the lower limit of crystallization threshold. However, following the demarcation temperature, the peak value and FWHM of Raman scattering monotonously closes to values of crystalline reference with annealing temperature, and increase in annealing time from 60 to 300 min further enhances these values much close to that of reference one. The FWHM shrinks with the increasing annealing temperature and time, which means the average size of crystal increases and the crystallinity gets improved and close to that of reference value of c-Ge..

Using peak analysis of Raman signal, crystalline fraction of the Ge thin films can be estimated [18]. Fig. 3 shows the calculated values of crystalline fraction for the films annealed at 300–500 °C for 60 and 300 min. As deposited α-Ge gradually reordering locally or may start to slightly crystallization in very small clusters with the increase in temperature up to 450 °C for 60 min. With the further increasing the temperature up to 500 °C, the Ge atoms could be activated to coalesce to form much bigger crystalline grains at the expense of small ones. In a one hour of annealing period the crystalline volume fraction of the films increases up to 87% for 60 min. It was observed that for the samples annealed at the same temperature, crystallinity noticeably enhanced with the annealing time from 60 to 300 min. At 450 °C, crystallinity increased from 30–78% for increasing annealing time whereas it was increased from 78–86% at 475 °C. Highest crystalline volume fraction was achieved with a percentage of 90% at 500 °C for 300 min.

Fig. 4 shows the XRD lines of the as-deposited and annealed samples for different annealing temperatures and times. Independent of the annealing time, no crystalline peaks were observed in the XRD patterns of the samples annealed at 400 °C and lower annealing temperatures as well as as-deposited one. When the annealing temperature increased to the value of 450 °C, two diffraction lines start to evolve at angles 27° and 45°, which are assigned to the diffraction from the planes Ge (111) and (220) respectively (Fig. 4(a) and Fig. 4(b)). At this temperature, increase in annealing time from 60 to 300 min makes these lines much more distinct and brings out emerging new diffraction peak from the Ge (311) plane (Fig. 4(b)). Further increase in