Raman Characterization of SiGe Nanostructures Formed by Rapid Thermal Annealing*

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This work presents the micro-Raman (µR) analysis in SiGe nanoclusters formed by rapid thermal annealing (RTA). Heterostructure of a-Si:H/Ge/a-Si:H was grown on p-Si (001) substrate by Electron Cyclotron Resonance ECR plasma deposition and e-beam technique. Different parts of the sample were heated at 1000°C during 40, 50, 60 and 70 seconds. The samples as-deposited and RTA processed were characterized by Raman measurements in order to evaluate the Ge concentration and strain for different annealing times. The same parameters were extracted from high-resolution x-ray diffraction (HRXRD) performed in grazing incidence x-ray reflection mode (GIXRR). The µR spectra were sensitive to film strain changes due to the Ge diffusion during RTA process. The association of both characterization techniques provides information about some features of the SiGe nanoclusters at different annealing times. The results show the potential micro-Raman applicability for SiGe nanoclusters embedded in amorphous structure characterization. [DOI: 10.1380/ejssnt.2009.301]

Keywords: SiGe nanoclusters; Rapid thermal annealing; High-resolution x-ray diffraction; Micro-Raman

I. INTRODUCTION

Amorphous Si₁₋ₓGeₓ has been studied as the basic material in high performance thin-film devices [1, 2]. An attractive factor in SiGe film is the compatibility with silicon based integrated circuits (IC). The fabrication of IC usually involves rapid thermal annealing (RTA) steps. The effects of thermal annealing in Si₁₋ₓGeₓ structures have been reported [3, 4]. Nakano et al. [5] studied the effect of thermal annealing on the Raman spectrum of Si₁₋ₓGeₓ grown on Si by very low pressure chemical vapor deposition (VLPVD). After annealing above 1000°C, was observed both Raman shift and the spectral shape, attributed to strong diffusion at this temperature. Nguyen-Duc et al. [6] show the SiGe nanostructures size increase after rapid thermal annealing at 900°C for durations of 1 s to 15 s. The low temperature process used suggests the rich SiGe samples. The effects of H₂ in SiGe samples during both growth and thermal annealing have been appointed. Xu et al. [3] observed the great increase of the growth rates during the first stages of the Ge island growth on H₂ preconditioned surface. Trinaksus et al. [7] studied the relaxation process of a Si₀.₈₅Ge₀.₁₅/Si(100) structure, grown by molecular beam epitaxy (MBE), as a function of annealing temperature. The H⁺ implantation and annealing with small residual dislocation densities was attributed to the production of a very high density of dislocation loops at the interface punched out by H filled nanocracks. These localized defects may form the nucleation cells for the nanostructures development. Usually, nanoislands have been grown using epitaxial techniques as both Chemical Vapor Deposition (CVD) and MBE [8–10]. Ritter et al. [11] reported the growth of Si-Ge materials via dehydrogenation of (H₃Ge)₃SiH₄ gas in the temperature range of 300-700°C. In the high temperature regime, was observed exclusive growth of self-assembled islands, or quantum dots formed spontaneously during the epitaxial growth. Recently, a-Si:H/Ge heterostructures were RTA processed to form Si₁₋ₓGeₓ nanostructures [12]. Was supposed that nanoclusters formation process from (H₃Ge)₃SiH₄ gas was partially reproduced in a-Si:H/Ge heterostructures RTA processed at 100°C. The low process time and the compatibility with IC technology indicates a potential a-Si:H/Ge RTA processed for semiconductor devices. However, the SiGe nanoclusters formed from this method need to be characterized for device applications. Different characterization techniques have been used in order to determine the nanoisland parameters as composition, strain and growth dynamic [13–15]. The most popular characterization techniques used to this goal are x-ray, Raman and Atomic Force Microscopy (AFM). Raman spectroscopy became a popular non-destructive technique for the determination of the Ge concentration (xGe) and strain (ɛ). Alonso et al. [11] studied the composition and strain profiles in Si₁₋ₓGeₓ islands grown on Si (001) by solid source MBE. Raman measurements were performed in order to support AFM and spectroscopy ellipsometry in etched samples for different times. However, the micro-Raman laser spot with 1 μm over the sample, approximately, detect the general sample features, i.e. film and nanoclusters together. X-ray measurements, on the other hand, provide crystalline nanocluster information. Information about the dynamic of the nanocluster formation may be obtained combining Raman and x-ray characterization techniques.

This work presents the micro-Raman (µR) spectra anal-
ysis in SiGe nanoclusters formed by RTA in a-Si:H/Ge heterostructures processed at 1000°C at different annealing times. The a-Si:H/Ge heterostructure was grown on p-type Si (001) and it is composed of 10 nm Ge layer sandwiched between two a-Si:H layers, both with nominal thickness of 40 nm. The a-Si:H layers were grown on Electron Cyclotron Resonance (ECR) plasma chemical vapor deposition and the Ge layer was grown on e-beam evaporation system. The μR measurements were supported by high-resolution x-ray diffraction.

II. SAMPLE GROWTH AND PROCESSING

The a-Si:H/Ge heterostructure was grown on p-type Si (001). The a-Si:H/Ge structure is composed of 10 nm Ge layer sandwiched between two a-Si:H layers, both with nominal thickness of 40 nm. The a-Si:H layers were grown on ECR using SiH₄ and Ar precursor gases. Their flows were set as 200 sccm and 20 sccm, respectively. The chamber pressure was kept at 4.0 mTorr. The Ge growth rate was 2 nm/min. The substrate temperature was 20°C and the growth rate was 13.34 nm/min., approximately. The Ge layer was grown on e-beam evaporation system. The operational chamber pressure was 6-7 Torr. The Ge growth rate was 2 nm/min. Then, the sample was carried out on ECR system again for 40 nm top layer growth of a-Si:H, reproducing the first a-Si:H layer. The sample was cleaved in five parts. Four sample pieces were RTA processed at 1000°C for 40, 50, 60 and 70 seconds and one was used as reference. The RTA was performed on RTP JIPELEC system model 150 Jetfirst in N₂ ambient, with a heating ramp of 50°C/s.

III. MICRO-RAMAN AND HRXRD CHARACTERIZATIONS

The samples processed by RTA and as-deposited one were characterized by μR measurements. The μR measurements were performed on a coupled micro-Raman and atomic force microscopy system NANOFINDER 30 at room temperature and using the 488 nm line with a power of 30 mW measured over the sample. The laser exposure sample time (~15 seconds) was controlled in order to reduce the heat effects in the Raman measurements. The unpolarized Ar Laser was focused perpendicularly on the deposited face of the sample with a spot of 1 μm of diameter, approximately. The scattered light was analyzed in a backscattering geometry using a monochromator-spectrograph MS5004i and CCD ANDOR DV401-BV detector. The focus on the sample was adjusted supported by a microscope OLYMPUS IX-71 just before each measurement. The most intense Si Peak determines the best focus. The final spectrum was obtained by integration of 10 successive measurements with 1 second each one.

The μR measurements were supported by HRXRD performed on GIXRR mode. The HRXRD measurements were performed on Philips X’Pert MRD with the CuKα radiation. The 0.5. Naturally, low angles provide more film information due the high penetration depth of CuKα₁ radiation. The both strain and xGe were calculated from Lorentzian fit spectra.

The xGe were estimated from GIXRR spectra peaks maximum position using the linear interpolation of the lattice constant known as Vegard’s Law. For diamond cubic Si-Ge the Vergard’s Law can be calculated using

$$x_{Ge} = (a_0(x) - 5.431)/0.226,$$

where $a_0(x)$ is the lattice constant of Si$_{1-x}$Ge$_x$. The average grain size was estimated using the Scherrer’s formula. The average of the three characteristics SiGe diffraction peaks were used for the average grain size estimation. The average strain was calculated using Stokes-Wilson formula, $\varepsilon = FWHM/(4\tan \Theta)$, where FWHM is the full-width half-maximum. The FWHM was determined from Lorentzian spectra fit peaks. Instrumental corrections were discarded in consequence of large measured broadening with instrumental broadening. Were estimated a variation of only 0.00001 arcsec in FWHM value applying instrumental corrections.

IV. RESULTS AND DISCUSSION

Figure 1 shows the μR spectra measured in samples annealed at 1000°C for 40, 50, 60 and 70 seconds and as-deposited one. The spectra of the as-deposited film show four characteristic peaks. The peak at 520 cm$^{-1}$, approximately, (partially visible) corresponds to longitudinal optical phonon vibrations of the Si–Si substrate bonds and can be observed in all spectra at same position. Three other peaks Si–Si layer, Si–Ge and Ge–Ge phonon modes located at 480, 400 and 280 cm$^{-1}$, respectively, are shown in the as-deposited μR spectra. The broad and smooth band nature of as-deposited Si–Si peak is characteristic of the predominantly amorphous structure. The Si–Si peak FWHM is diminished with annealing time, indicating that the Silicon crystalline quality increases after annealing. However, the Si–Ge peaks showed the opposite behavior. This was attributed to diffusion of Germanium into silicon layers induced by RTA process. At 1000°C the Ge is melted and the characteristics observed in as-deposited spectra were changed. The Ge–Ge peak was collapsed after RTA processing. This fact indicates that the Ge–Ge bonds were completely cracked forming Si–Ge and Ge–H bonds after annealing.

The intermixing of Ge and a-Si:H change the film strain. This effect is noted in μR spectra by the peaks shift. In order to evaluate the strain changes promoted by different RTA process times in comparison with as-deposited sample, both Si-Si and Si-Ge Raman shift were plotted as function of annealing time, as shown in Fig. 2. The Si–Si layer peak is shifted according to the annealing time, as shown in Fig. 2(a). The sample RTA processed for 40
FIG. 1: Micro-Raman spectra for RTA processed for 40, 50, 60 and 70 seconds and as-deposited sample. 

seconds presents a left shift in Si–Si layer peak of the 3 cm$^{-1}$, approximately, compared with as-deposited film. As the RTA time increases, the Si–Si layer peak position dislocates to higher wavenumber values, as shown in Fig. 2(a). This behavior is associated to strain increase by Ge diffusion in the a-Si:H layers. However, only for high annealing times the Ge diffusion increased the a-Si:H strain layer, comparing with as-deposited sample. Localized defects as crack-like cavities induced by RTA process at high temperatures contribute to strain increase too. This hypothesis is supported by the deviations from the linear behavior of Raman shift with composition and strain. However, the limited number of samples is not conclusive about the linear behavior. The similar shift of the Si–Ge with Si–Si peaks according to the annealing time, shown in Fig. 2(b), suggest the interdiffusion of Si and Ge layers. Therefore, the Raman shift is supposed predominantly caused by strain more than concentration changes. In order to evaluate this hypothesis strain and Ge concentration values were calculated using the $\mu R$ spectrum. 

Empiric models devoted to determinate the dependences on composition $x$ and in plane strain $\varepsilon$ of the SiSi, SiGe, and GeGe phonon frequencies $\omega$ have been reported [16–18]. Some studies are based on relative intensities of Raman peaks to determinate the film composition. In this case, is assuming that the relative number of the bonds of Si–Si, Si–Ge and Ge–Ge are proportional to respective peak intensities. The number of the bonds depends on the composition $x$ as follow. $N_{GeGe} = x^2$, $N_{SiGe} = 2x(1-x)$, $N_{SiSi} = (1-x)^2$. The relative intensities of the Raman peaks is expressed as follow. $I_{GeGe}/I_{SiGe} = Bx/2(1-x)$, $I_{SiSi}/I_{GeGe} = A(1-x)/2x$. The parameters $A$ and $B$ can be extracted using the film composition determined from another technique as x-ray or EDS (Energy Dispersive Spectroscopy). However, a number of samples with different composition are suitable for accurately determinate $A$ and $B$. Another point to be considered in this case is the Ar laser penetration depth. The crystallization promoted by RTA process at different times may change the penetration depth, particularly in the case of the 488 nm laser, complicating the analysis between samples. The characteristics of our samples are not compatible with this method. The empiric model to determinate the composition based on position of the Raman peaks was used here. The empirical formulae used for the determination of the Ge concentration and strain in SiGe systems have been extensively reported [3, 19, 20]. Tsang et al. [21] showed the Raman spectroscopy ability to simultaneous determination of composition and strain in thin SiGe layers. The authors investigated four methods. One of them determinate the composition and strain based on Raman frequencies using the empirical formulae. The samples were growth by ultrahigh vacuum CVD and were highly homogeneous. Groenen et al. [22] used the Raman frequencies method in strained SiGe islands grown by liquid phase epitaxy. The method applicability for SiGe nanoislands is supported by the considerably large Raman spot than SiGe island size. In consequence, the spectra correspond to an average over an island ensemble. This fact motivated the use of the Raman frequencies method here. In our case, the average crystalline grain size calculated from the x-ray mea-

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measurements suggest the grain size much lower than Raman spot too. Energy dispersion X-ray spectroscopy (EDS) measurements were performed in order to verify the uniformity of our samples. Scans with 1 μm per diameter on both different areas and samples showed no content variation. The results were sufficient to apply the empirical formulae. However, the empirical formulae application in samples with identical characteristics as studied here were not found. This is a relevant contribution to this work for Raman characterization. The composition $x$ and in-plane strain $\varepsilon$ of the SiSi, SiGe, and GeGe phonon frequencies $\omega$ can be written as

$$\omega_{\text{SiSi}} = 520.5 - 62x - 815\varepsilon, \quad (1)$$
$$\omega_{\text{SiGe}} = 400.5 - 14.2x - 575\varepsilon, \quad (2)$$
$$\omega_{\text{GeGe}} = 282.5 + 16x - 385\varepsilon. \quad (3)$$

The Eqs. (1) and (2) were used to determinate the $x_{\text{Ge}}$ and strain in the samples RTA processed during 40, 50, 60 and 70 seconds. The $x_{\text{Ge}}$ based on µR spectra shows almost constant values at 10% for different annealing times. Coherently, these values are close to the nominal concentration at 11% estimated for the as-deposited sample, calculated based on the nominal layer thickness. This fact agrees with the hypothesis of the Raman peak shift to be dependently of strain changes predominantly. However, the GIXRR structural characterization showed the $x_{\text{Ge}}$ increase in the crystalline nanoclusters according to annealing time. Figure 3 shows the $x_{\text{Ge}}$ calculated from µR spectra (open circles) and calculated from GIXRR spectra (full circles) as a function of annealing time. The GIXRR $x_{\text{Ge}}$ values increase from 8 to 19% with the annealing time. Based on GIXRR $x_{\text{Ge}}$ values two hypothesis for nanocluster dynamic with the annealing time can be appointed: 1) The $x_{\text{Ge}}$ in nanocluster increase due the Ge incorporation from the amorphous structure or 2) The $x_{\text{Ge}}$ in nanocluster increase due the Si extraction from the nanoclusters. The second hypothesis is supported by the nanocluster diminishing according to annealing time reported in a previous work [23] calculated from GIXRR measurements.

The average grain size calculated from GIXRR measurements varied from 3.5 nm to 7.5 nm with the annealing time. The plotted nanoclusters strain, extracted from GIXRR, versus the film strain, extracted from Raman measurements, is shown in Fig. 4. The inversely proportional and quasi-linear behavior in the samples RTA annealed for 40, 50, 60 and 70 seconds was observed. This result appointed the nanoclusters strain increases while the amorphous film is relaxed. This fact is coherent with the silyl radical diffusion from the SiGe nanoclusters to a-Si:H/Ge after RTA process. The RTA process induce the Ge diffusion in a-Si:H layers forming SiGe nanocluster on substrate and bubbles on surface samples. The nanoclusters were formed by solid-phase crystallization of the SiGe on substrate. Some Ge content was not crystallized forming both secondary compords of SiGe and Ge. Accurate techniques are suitable to a satisfactory morphological model. AFM, EDS and SEM measurements have been performed in our samples and the results, associated with results exposed here, will provide a complete morphological model to be published as soon.

V. CONCLUSIONS

Micro-Raman and x-ray measurements in GIXRR mode were performed in Si$_{1-x}$Ge$_x$ nanoclusters formed by RTA process at 1000°C for annealing times of 40, 50, 60 and 70 seconds. The Ge concentration calculated from micro-Raman spectrum peak position was coherent with nominal values and the peak shift was dominated by strain changes during RTA process. These results show the potential micro-Raman applicability for SiGe nanoclusters.
embedded in amorphous structure characterization. However, the micro-Raman technique showed the general features of the film and need to be associated with another characterization technique. The specific technique choice will depend on the previous knowledge of the film characteristics. In our case, the x-ray characterization was important to extract the nanoclusters crystalline information. The association of both characterization techniques was able to identify some features of the SiGe nanoclusters at different annealing times. For example, the Ge concentration increase in crystalline nanoclusters, measured by GIXRR was attributed to silyl radicals extraction during the RTA process. This fact was observed in inversely proportional behavior of the strain measured from both techniques. However, the specific formulations for Ge concentration and strain calculations based on micro-Raman spectra want to be developing in order to obtain refined results in SiGe nanostructures embedded in amorphous structure. This is possible using techniques as EDS associated with micro-Raman analysis.

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