ORIGINAL ARTICLE

The Improving $Si_{0.5}Ge_{0.5}/Si$ Interface Quality through a Low Energy Hydrogen Plasma Cleaning Process and Positron Annihilation Spectroscopy

Cho-Fan Hsieh[1], Chen-Wei Chen[1], Chih-Hua Chen[1,2], and Ming-Han Liao[2,*]

[1] *Industrial Technology Research Institute (ITRI), Taiwan*

[2] *Department of Mechanical Engineering, National Taiwan University, Taiwan*

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*Corresponding author: mhliaoa@ntu.edu.tw

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Abstract: Positron Annihilation Spectra (PAS), Raman, and photoluminescence spectroscopy reveal that $Si_{0.5}Ge_{0.5}/Si$ interface quality can be dramatically improved through a low energy plasma cleaning process using hydrogen. In the PAS, the particularly small values of lifetime and intensity near the $Si_{0.5}Ge_{0.5}/Si$ interface in the treated sample indicate a 2.25 times reduction in defect concentration. Fewer defects were found in the interface, resulting in a high compressive strain of about 0.36 % in the top layer, which can be observed in Raman spectra, and a 1.39 times increase to the radiative recombination rate for the infrared emission, which can be observed in the photoluminescence spectra. Improved $Si_{0.5}Ge_{0.5}/Si$ interface quality leads to improved optical and electrical characteristics in SiGe-based devices in a broader range of photovoltaic applications. The PAS is also shown to be a useful metrology tool for quantifying defects in SiGe-based devices.

Keywords: Defect, Low energy hydrogen plasma cleaning process, SiGe-based devices, Positron annihilation spectroscopy

Introduction

Recently, SiGe solar cells have attracted considerable research interest due to their strong photon absorption [1], high light emission efficiency [2], high carrier mobility [3], and possible integration with Si. One key issue for the practical application of SiGe-based devices is the interface quality between the epi-SiGe layer and Si substrate. In previous studies, we used Raman spectroscopy [4-6] and electroluminescence spectroscopy [7] to respectively investigate the Si/Ge diffusion model [8] and monitor the Ge/Si interface quality. Positron Annihilation Spectra (PAS) [9] is a useful metrology tool from organic material engineering for extracting defect information including defect size and concentration [10]. In this work, we quantitatively extract and analyze defect information from $Si_{0.5}Ge_{0.5}/Si$ samples using PAS, photoluminescence (PL), and Raman spectroscopy. Results indicate that interface quality can be significantly improved by using low energy plasma cleaning (LEPC) with hydrogen prior to the deposition of the epi-SiGe layer, thus reducing defect concentrations near the interface. LEPC has multiple effects on the substrate and the grown layer. It effectively removes the native silicon dioxide and hydrocarbons, resulting in a clean silicon surface terminated with hydrogen atoms [11-13]. In previous studies, extending the Si in situ surface treatment to Ge and Si/Ge surfaces demonstrated results consistent with related research in silicon [14]. Reduced interface defects in the $Si_{0.5}Ge_{0.5}/Si$

sample leads to stronger radiative infrared emission in the PL spectra, an increased (0.36 %) $Si_{0.5}Ge_{0.5}$ compressive stress in the Raman spectra, and a lower Doppler (S) value in the PAS.

Experiment

The samples studied in this work consist of an epi-$Si_{0.5}Ge_{0.5}$ (~30 nm) layer on a Si substrate, which is grown by ultra-high-vacuum chemical vapor deposition (UHV/CVD) at 525 ^{o}C using the Stranski-Krastanov (SK) growth mode [7]. SK growth mode is a low temperature process and a detailed explanation of the growth mechanism and process conditions can be found in Ref. [7]. Prior to the deposition of epi-$Si_{0.5}Ge_{0.5}$ layer on the Si substrate, the substrate is cleaned using modified residual gas analysis (RCA): 10 min at 70 ^{0}C in 5:1:1 H_2O:H_2O_2:NH_4OH for organic, particulate, and heavy metal contamination; and 10 mins at 70 ^{0}C in 5:1:1 H_2O:H_2O_2: HCl for ionic contaminants, with intermediate HF dips and DI rinses. The Si substrate used in this work is an N-type substrate with a doping level of 10^{15} cm^{-2}. To remove as much of the native oxide as possible, a final dilute 1:40 HF: H_2O dip is followed by a 30-s DI water rinse and drying in N_2, prior to wafer loading into the vacuum chamber. The RCA clean followed by the HF dip has consistently produced the best results to date. Sample A is the control without LEPC treatment, while Sample B is the experimental sample with LEPC treatment. For the LEPC process, the in situ cleaning of the Si surface is achieved by plasma excited H_2. The H_2 can be introduced either through the plasma column for remote plasma excitation or through the gas dispersal ring for indirect excitation by Ar or He atoms using remote plasma excitation. Remote plasma excitation of hydrogen produced excellent in situ cleaning results. The LEPC process used hydrogen in situ cleaning parameters including a hydrogen flow rate of 100 sccm, a hydrogen partial pressure of 30 mTorr, an RF power of 50 W, and a substrate temperature of 300 ^{0}C. In the process, the hydrogen can act as a surfactant during the growth of SiGe, suppressing the formation of Ge islands on the substrate. During the evolution of SiGe films on Si (001) substrates the adsorbed atomic hydrogen effectively suppresses the clustering of SiGe and defect formation. Although the thickness range (~30 nm) used here is beyond the critical thickness predicted by the Matthews–Blakeslee theory, one should note that, in this work, the misfit dislocations are kinetically inhibited due to the low growth temperature of hydrogen-surfactant epitaxy [8].

Cho-Fan Hsieh, working for Industrial Technology Research Institute of Taiwan.

Chen-Wei Chen, working for Industrial Technology Research Institute of Taiwan.

Chih-Hua Chen, received the B.S. degree in mechanical engineering and the M.S. degree in opto-mechatronics engineering from the University of Science and Technology of China. He is currently working toward the Ph.D. degree at National Taiwan University, Taipei, Taiwan.

Ming-Han Liao, associate professor in the department of mechanical engineering, National Taiwan University, Taipei, Taiwan, R. O. C.

Positron annihilation, PL, and Raman spectroscopy are used to analyze and quantify the defect information near the SiGe/Si interface.

For the PAS measurement, positrons in the energy range from 0 to 30 keV were implanted in our two samples: Sample A (without the treatment) and Sample B (with the treatment) before the deposition of the epi-$Si_{0.5}Ge_{0.5}$ layer. A conventional fast coincidence spectrometer with a time resolution of 250 ps was used for PAS measurements. The positron source (10 μCi) ^{22}Na was deposited in an envelope of Kapton foils (6 μm thick) and then sandwiched in between a sufficient thickness of each sample. One million counts were recorded for each PAS spectrum for a typical period of acquisition of 3~5 h. The conventional analysis used the PATFIT-88 program. Source correction terms were made from each spectrum in data analysis [9, 10].

The slow positron is calibrated and its performance is as good as or better than that of existing radioisotope beams: its conversion efficiency = 6 x 10^{-4} and beam diameter < 5 mm using a PC-controlled focus for positron energies 0-30 keV. The S parameter of Doppler energy broadening spectroscopy (DBES) represents the relative value of the free volume depth profile in our sample (defined as the ratio of the low momentum part of the peak region to the total 2τ annihilation near 511 keV energy).

For the Raman measurement, a 488 nm line of argon laser was used as the excitation source to investigate the Ge composition and strain effect in our epi- SiGe layer [7]. The laser beam was focused on the sample surface with a spot size of ~1 μm. Backscattering light was collected and recorded by a triple grating spectrometer with a liquid nitrogen-cooled charge coupled device. The Raman spectra have a resolution of 0.2 cm^{-1} and the Lorentzian line shape was used to determine the peak position of the line shape. In the theoretical calculation, the Ge-Ge peak of SiGe samples shifts towards the positive axis under the compressive strain [6, 15]. The Raman shift of 3 cm^{-1} was extracted from the curve fitting using Lorentian profile, corresponding to the biaxial compressive strain of ~0.36 % in the $Si_{0.5}Ge_{0.5}$ under the theoretical calculation [6, 15].

For the PL measurement, the samples were excited by light with a wavelength of 325 nm from a He–Cd laser of ~50 mW focused on a circular area with a radius of ~1 mm. Analysis was conducted using an NIR spectrometer (NIRQuest512 Ocean Optics) and the electron-hole plasma recombination model [7].

Results and Discussions

Figures 1 (a) and (b) respectively show the cross-section transmission electron microscopy (TEM) images for the two samples, consisting of an epi-$Si_{0.5}Ge_{0.5}$ (~30 nm) layer on the Si substrate, without and with the LEPC process using hydrogen prior to the deposition of the epi-$Si_{0.5}Ge_{0.5}$ layer. In the control sample A, the lattice mismatch between the interface is about 2 %, leading to serious defects and a dislocation line near the interface as shown in Figure 1 (a). In Sample B, the interface quality is considerable improved as observed in Figure 1 (b). No defects or dislocation line is found near the interface with the treatment. This observation is also confirmed by TEM images produced using the weak beam method. The nearly perfect SiGe/Si interface in Sample B indicates increased compressive stress in the epi-SiGe layer, which confirmed by Raman spectra analysis.

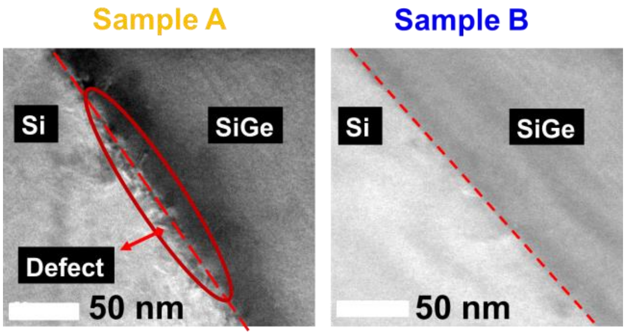

Figure 1. Cross-section transmission electron microscopy (TEM) images for samples with/without the LEPC process treatment using hydrogen.

To quantify the defect type and concentration in these two samples, DBES [9] testing results are shown in Figure 2. In Sample B, the smaller S parameter indicates that Sample B with the LEPC process treatment indeed has fewer defects and a better layer quality than Sample A. The spectra of the positron lifetime are measured from 0 to 30 keV and then decomposed into two components. Figure 3 (a) shows the experimental results. By using the derived values, we could estimate the lifetime of a positron from the free state, τ_b as about 230 ps in our SiGe samples. On the other hand, the derived defect lifetime, τ_d, is found to be close to the lifetime of trapped positrons at about 340 ps. The defect concentration [16] along the sample depth direction for these two samples can be extracted using the formulas shown below and the results are shown in Figure 3 (b).

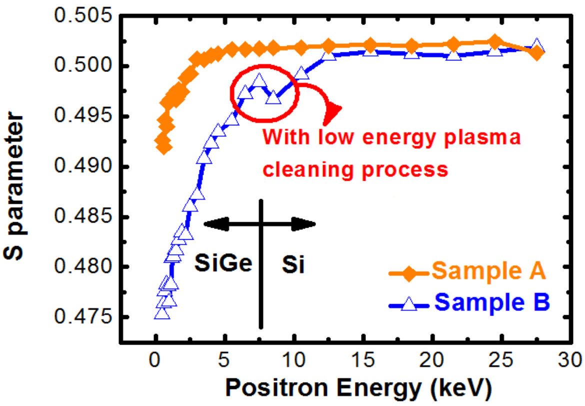

Figure 2. Doppler broadening energy spectroscopy (DBES) for the samples with/without the LEPC process treatment using hydrogen.

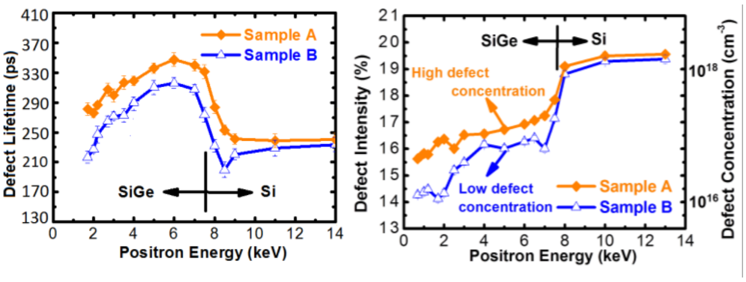

Figure 3. (a) Defect lifetime and (b) extracted defect concentration in our two samples. The defect concentration near the SiGe/Si interface with the LEPC process treatment using hydrogen is reduced from 4.5 x 10^{17} cm^{-3} to 2 x 10^{17} cm^{-3} (about 2.25 times).

In this work, we assume the positron is first captured in a single open-volume. According to the one-defect trapping model [9], two lifetimes (τ_b and τ_d) can be extracted in the experimental lifetime spectrum:

$$\tau_b = \frac{1}{\lambda_b + k_d}, \quad \tau_d = \frac{1}{\lambda_d}, \quad I_b = 1 - I_d, \quad I_d = \frac{k_d}{\lambda_b - \lambda_d + k_d}, \quad (1)$$

where λ_b is the positron annihilation rate in a perfect defect-free crystal and λ_d = $1/\tau_d$ is the positron annihilation rate in a trapped (localized) state. k_d is the positron trapping rate of the defect. I_d and I_b respectively show the experimental defect lifetime intensity and theoretical material bulk lifetime intensity.

The τ_d is the reciprocal of the positron annihilation rate in the defective sample and is not dependent on the defect concentration (Equation 1). Information about the electron density at the annihilation site can be extracted by τ_d. Therefore, it can be used as a characteristic value for the open volume of the defect. In the semiconductor material, the ratio of τ_d/τ_b for the mono-vacancy is about 1.2. The defect concentration is proportional to the value of k_d:

Defect concentration [16]: $$\mu C = \frac{I_d}{I_b} \times \left(\frac{1}{\tau_b} - \frac{1}{\tau_d} \right). \quad (2)$$

Where μ and C are respectively the theoretical trapping coefficient and the extracted defect concentration. The value of the related parameters is covered in [9].

The maximum point of the defect concentration in the epi-SiGe layer is located at the SiGe/Si interface while the minimum point is on the top surface of the epi-SiGe layer. This indicates that the SiGe/Si interface plays a critical role in thin film technology, consistent with the TEM image observations in Figure 1. Note that the positron energy shown in Figure 3 ranges from 0 keV to 14 keV. The energy level used in this work is designed to extract the defect information near the SiGe/Si interface.

Results show that the defect concentration at the SiGe/Si interface with the LEPC process treatment can be reduced from 4.5×10^{17} cm^{-3} (sample A) to 2×10^{17} cm^{-3} (sample B). Applying the LEPC process treatment prior to depositing the epi-SiGe layer on the Si substrate indeed reduces the defect size and concentration near the SiGe/Si interface, and improves the SiGe/Si interface quality. Positron Annihilation Spectra (PAS) [9] is shown to be a useful metrology tool for extracting defect information, and its spatial resolution was shown to be within 0.1 Aring (Å) level [9] due to the increased excitement of the nuclear energy of the light source.

In addition to the PAS, Raman and PL spectrum are two additional optical morphology tools which can extract defect information in semiconductor materials. Figure 4 shows the Raman spectra of both samples. Aside from the strong Si signal at 520 cm^{-1}, Ge–Ge 2TA(X) [6] phonon and Si–Ge 2TA(L) [6] phonon of the epi SiGe layer were also observed. The Si–Ge 2TA(L) phonon signal ~221 cm^{-1} is insensitive to strain and is a strong function of Ge composition [6] while the Ge–Ge 2TA(X) phonon peak about 300 cm^{-1} is sensitive to both strain and Ge composition. Based on experimental results of the Si–Ge 2TA(L) phonon node in $Si_{1-x}Ge_x$ alloys, the wave number at 221 cm^{-1} indicates that the average Ge composition is 53 % for both samples. On the other hand, the larger Raman frequency shift (~ 3 cm^{-1}) of the Ge-Ge 2TA(X) phonon peak at around 300 cm^{-1} in Sample B. Figure 4 shows Sample A suffered 0.36% more compressive strain than Sample B (with the same Ge concentration ~53%). This indicates that the epi-$Si_{0.5}Ge_{0.5}$ layer quality in Sample B with the LEPC process is better than that in Sample A. In Sample B, the increased compressive stress in the epi-$Si_{0.5}Ge_{0.5}$ layer results in reduced lattice mismatch between the SiGe and Si substrate, thus improving SiGe quality. The experimental results for TEM, DBES, and Raman spectra are consistent in this regard.

In the theoretical calculation, the Raman phonon strain-shift coefficient (b) with the biaxial stress treatment in the epi-$Si_{0.5}Ge_{0.5}$ layer is ~838 cm^{-1}/strain [15]. In the theoretical extraction and calculation, the Raman shift of 3 cm^{-1} corresponds to the biaxial compressive strain of ~0.36 % in the $Si_{0.5}Ge_{0.5}$ [6, 15].

Moreover, Sample B, with its improved SiGe/Si interface quality, has a higher PL intensity (~1.39 times as shown in the Figure 5) than Sample A on the ~1.1 μm Si light emission signal and exhibits no dislocation line energy (D1-D4) in the PL spectra. The reduced number of defects in the SiGe/Si interface results in increased PL intensity due to the reduced non-radiative recombination center for the electron in the conduction band and the hole in the valence band. The TEM images show that the SiGe/Si lattice mismatch induced defect near the interface between the epi-SiGe layer and Si substrate. Thus the ~1.1 μm Si PL signal from the SiGe/Si interface reflects the quality of the epi-SiGe layer. The three morphology tools (PALS, Raman, and PL) all confirm the improved SiGe/Si interface quality resulting from the LEPC process with hydrogen treatment in Sample B.

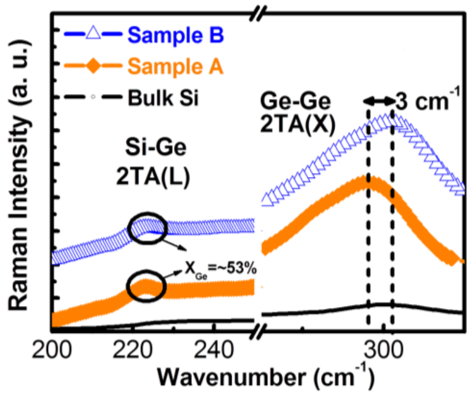

Figure 4. Raman spectra on two tested samples. The larger Raman frequency shift (about ~ 3cm^{-1}) of the Ge-Ge phonon in Sample B with the LEPC process treatment using hydrogen.

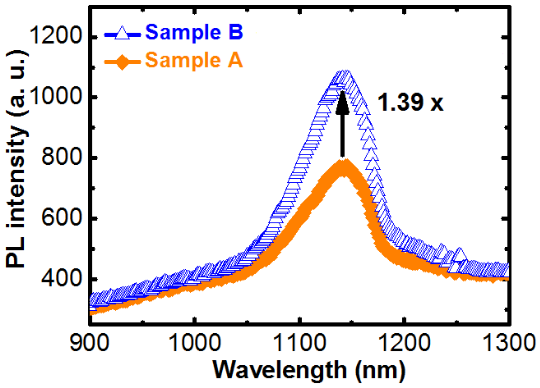

Figure 5. PL spectra on two tested samples. Sample B, with improved SiGe/Si interface quality, has a PL intensity about 1.39 times greater than Sample A.

Conclusion

The LEPC process treatment using hydrogen can significantly improve the quality of the $Si_{0.5}Ge_{0.5}/Si$ interface. The PALS spectra show that, with the treatment, the defect concentration near the $Si_{0.5}Ge_{0.5}/Si$ interface can be reduced from 4.5 x 10^{17} cm^{-3} to 2 x 10^{17} cm^{-3}. The high compressive strain (~0.36 % strain) in the epi-$Si_{0.5}Ge_{0.5}$ layer observed in the Raman spectra indicates the good interface quality of the top epi-$Si_{0.5}Ge_{0.5}$ layer, thus increasing the radiative infrared emission in the PL spectra. This increased SiGe/Si interface quality is conducive to the development of SiGe-based optical and electrical devices for a broader range of important photovoltaic industrial applications. Positron Annihilation Lifetime Spectra (PALS) is also demonstrated as a useful metrology tool to extract defect information in SiGe-based devices.

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