Surface Detection of Strain-Relaxed Si$_{1-x}$Ge$_x$ Alloys With High Ge-Content by Optical Second-Harmonic Generation

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Abstract—We investigated the strain and surface structural properties of a strain-relaxed Si$_{1-x}$Ge$_x$ alloy layer with high Ge-content using optical surface second-harmonic generation. Here, the Si$_{1-x}$Ge$_x$ alloys are heteroepitaxial, and they are deposited onto Si substrates via ultra-high-vacuum-chemical vapor deposition. The in-plane strain and the composition $x$ of the Si$_{1-x}$Ge$_x$ alloys were determined using Raman spectroscopy. The SH signals generated from three Si$_{1-x}$Ge$_x$ alloy surfaces versus the rotational angle of the substrate were measured. The SH intensities for the combination of s-input/p-output polarization show fourfold symmetry; however, for s-input/s-output, the SH signals show eightfold symmetry with the rotational angle. Residual strain would induce an enhancement of the isotropic p-output SH component in the Fourier transform coefficient. Finally, the degree of symmetry of the SH signals from these three Si$_{1-x}$Ge$_x$ alloy surfaces versus the rotational angle was related with the surface pit defects (densities and sizes) and surface roughness.

Index Terms—Femtosecond laser, Si$_{1-x}$Ge$_x$ alloys, second-harmonic generation, strain-relaxation, surface defects.

I. INTRODUCTION

Ge-RICH SiGe alloys have attracted the comprehensive attention of many researchers in the microelectronic and optoelectronic industry due to the possible enhancement of carrier mobility in metal oxide semiconductor field effect transistor channels enabled by these materials and their absorption in the near-infrared for wavelengths up to 1.55 μm [1]–[7]. As is known, however, the heteroepitaxy of Ge-rich SiGe alloy layers directly on Si is complicated by the large lattice mismatch between Si and Ge. To overcome this problem, intermediate layers are inserted between the Si substrate and the desired high Ge content SiGe alloys. Here, the strain of intermediate layers deposited onto the Si substrate is relaxed due to the insertion of dislocations after an adequate thickness; such layers are so-called strain-relaxed SiGe alloys [8], [9]. The quality of the strain-relaxation layer (especially for the surface), such as the degree of strain-relaxation and the density of defects in the surface of the SiGe alloy layer, would evidently affect the quality of the materials that grow on them. However, the strain and surface defects in an alloy layer can change the structural symmetry of the SiGe alloy, or in other words, they can affect the second-order nonlinear susceptibility of the SiGe alloy. Thus, the strain and surface defect in a SiGe alloy layer are also sensitive to the surface second-harmonic generation (SSHG) technique, an in-situ and contactless optical detection method. Specifically, the structural information for dozens of atomic layers in the surface can be obtained using a near-infrared femtosecond laser pump [10]–[16]. Therefore, in this work, the SSHG technique is used to investigate the strain and surface defect behavior in high Ge content Si$_{1-x}$Ge$_x$ alloy layers.

II. EXPERIMENTS

The strain-relaxed Si$_{1-x}$Ge$_x$ alloy samples used in this work are prepared by ultra-high-vacuum - chemical vapor deposition (UHV-CVD), with Si$_2$H$_6$ and GeH$_4$ gases as the reactive source materials [17], [18]. Three Ge content Si$_{1-x}$Ge$_x$ alloy layers on Si (001) substrates are prepared: these samples are marked as A, B and C. Before the growth of the Si$_{1-x}$Ge$_x$ alloy layers, a low-temperature buffer layer was inserted between the alloy film and the Si substrate. The growth conditions of the low temperature Ge layer and the Si$_{1-x}$Ge$_x$ alloy layers of three samples are listed in Tab. 1. The thicknesses of the low-temperature Ge layer are 10 nm for sample A, 20 nm for sample B, and 50 nm for sample C, respectively. In order to avoid causing island in thin Ge buffer layer and improve...
quality of the Si$_{1-x}$Ge$_x$ alloy layer, growth temperature of the Si$_{1-x}$Ge$_x$ alloy was raised to 600 °C by method of fractional steps. The thickness of all three alloy layers is approximately 600 nm, and the density of dislocations for these samples is approximately $10^5$–$10^6$ cm$^{-2}$ measured by etch-pit density counting (EPD) method [27], [28]. To induce an intensive SH field with a high signal-to-noise ratio, a Ti:sapphire femtosecond (fs) oscillator with an 800-nm wavelength is used as the fundamental light (s-polarized, repetition frequency of 80 MHz, and pulse width of 120 fs) [11]. The s-polarized beam is focused by a lens onto the surface of Si$_{1-x}$Ge$_x$ alloy samples at a 45° angle of incidence with respect to Si (100) direction. Further, the SH signal is filtered by a saturated CuSO$_4$ solution and then by an interference filter of 405 nm. Finally, the SH signal is focused into a photomultiplier tube, and the generated electrical signal is detected using a lock-in amplifier. The SSHG experimental setup show as Fig. 1.

To study the rotational angle SHG (RA-SHG), the p- and s-polarized SH is selected using a polarization analyzer. In the experiments, the samples can rotate around their normal direction or the central axis of the rotational stage. A computer was employed to synchronously control a stepper motor to rotate the sample and obtain data of the SH signal from the lock-in amplifier.

III. RESULTS AND DISCUSSION

The composition, $x$, and strain field, $\varepsilon$, of the samples were measured by means of Raman spectroscopy. The Raman spectra of three samples with a 633-nm excitation wavelength are shown in Fig. 2. The Raman spectrum of Si$_{1-x}$Ge$_x$ alloys is dominated by two main peaks corresponding to the Si-Si, Ge-Ge, and Si-Ge nearest neighbor vibrations. Following the work of Pezzoli and co-worker [19]–[21], the strain $\varepsilon$ and composition $x$ of the Si$_{1-x}$Ge$_x$ layers can be determined by solving the following algebraic system:

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\begin{align*}
\omega_{\text{Si-Ge}}(x, \varepsilon) & = \omega_{0}\text{Si-Ge} + 25.4x - 4.5x^2 - 33.5x^3 + b_{\text{SiGe}}\varepsilon, \\
\omega_{\text{Ge-Ge}}(x, \varepsilon) & = \omega_{0}\text{Ge-Ge} + 19.4x + b_{\text{GeGe}}\varepsilon
\end{align*}
\]

(1)

where the expressions $(\omega_{0}\text{Si-Ge} + 25.4x - 4.5x^2 - 33.5x^3)$ and $(\omega_{0}\text{Ge-Ge} + 19.4x)$ represent the values of the Si-Ge and Ge-Ge mode frequencies in the unstrained Si$_{1-x}$Ge$_x$ alloy, respectively. The values of $\omega_{0}\text{Si-Ge}$ and $\omega_{0}\text{Ge-Ge}$ equal 400.1 cm$^{-1}$ and 280.3 cm$^{-1}$, respectively. Additionally, the value of the Ge-Ge mode frequency that was calculated using expression $(\omega_{0}\text{Ge-Ge} + 19.4x, \text{for } x \to 1)$ in the Si$_{1-x}$Ge$_x$ alloy is in agreement with the experimental results obtained from the Raman spectroscopy of a Ge crystal wafer (299.7 cm$^{-1}$). The $b$ values are phenomenological parameters dependent on the elastic constants of a given material, which are independent of $x$ in the composition range considered in this work. Their values were taken from Refs. [19], [20]. From Fig. 2 and Eqs. (1), the composition $x$ and strain $\varepsilon$ of the three samples can be calculated, as listed in Tab. 2.

For SH detection, the s-polarization is selected as the input fundamental light, and the p- and s-polarized SH signals are measured. The dependence of the s-in/p-out SH intensity on the rotational angle of the three samples is shown in Fig. 3.
The p-polarized SH output curves show four-fold symmetry for all three Si$_{1-x}$Ge$_x$ alloy samples. The curves in Fig. 3 are then fitted by the following expression [10], [22]:

$$I_{k}^{(2\omega)}(\phi) \propto \sum_{m=1}^{4} \left\{ a^{(m)} \cos(m(\psi + \phi)) + b^{(m)} \sin(m(\psi + \phi)) \right\}^2 + h$$

(2)

where $\phi$ is the angle between the plane of incidence and the Si (110) direction, $I_{k}^{(2\omega)}$ is the SH intensity ($g$ represents the s- or p-polarized output SH), and the polarization state of the input fundamental light is s-polarized. Note that in Tab. 3 and in the following, $C^{(m)} = \sum_{g} a^{(m)} + b^{(m)}$ is defined as in Ref. 10. Using Eq. (2) as the fitting formula, the fitting curves are shown as solid lines in Fig. 3. After being normalized with $C^{(0)}$, the fitted Fourier coefficients of each item of the s-in/p-out polarization are shown in Tab. 3. The constant item $h$ in Eq. (2) corresponding to the isotropic SH contribution [23].

The $C^{(0)}$ coefficient from Eq. (2), which leads to an isotropic response, mainly arises from the strain-enhanced interface effect; the $C^{(4)}$ coefficient results from bulk quadruple sources. From Tab.3, we find that $C^{(0)}$ are the largest Fourier coefficients for s-in/p-out; i.e., the strain-enhanced effect is the main contribution to the SH signal for all three samples, but the bulk dipole allowed contributions ($C^{(2)}$) are very small. For the three Si$_{1-x}$Ge$_x$ alloys, a residual strain of 0.01 remains in the strain relaxed alloy layers; thus, the strain-enhancement effect is present.

Next, the dependence of the s-in/s-out SH intensity on the rotational angle is also measured, and the results are shown in Fig. 4. Fig. 4 (a) shows that the SH intensity vs the rotational angle exhibits eightfold symmetry for all three SiGe alloy samples. The s- and p-out RA-SHG from the Si$_{1-x}$Ge$_x$ alloy (100) exhibit different symmetries, which can be explained by the phenomenological theory of optical SHG from a cubic crystal [25]. Additionally, the eightfold symmetry of the s-out RA-SHG from the strain-relaxed Si$_{1-x}$Ge$_x$ alloy did not change significantly as a result of the small strain [11], [22]. Similarly, the experimental curves are fitted by Eq. (2), and the Fourier coefficients of each item for the s-in/s-out polarization are shown in Tab. 3. The results are different from those of the s-in/p-out SH, as $C^{(4)}$ is the largest Fourier coefficient; i.e., the bulk quadruple contribution is dominant in this polarization combination. From the Fourier transform patterns in Fig. 4 (b), the effect of $C^{(4)}$ induced by the bulk quadruple is remarkable.
characterized using an atomic force microscope (AFM), and the AFM images for the three SiGe alloys are shown in Fig. 5.

From Fig. 5, it is apparent that surface pit defects created by the strain relaxation (are different from dislocation-bulk defects) are present both in the Si0.26Ge0.74 alloy and the Si0.20Ge0.80 alloy. Information regarding the parameters of the surface pit defects are listed in Tab. 4. For the Si0.26Ge0.74 alloy, the density of pits with a 51.1-nm mean depth is $4.5 \times 10^7$, and for the Si0.20Ge0.80 alloy, the density of pits with a 30.5-nm mean depth is $8.0 \times 10^6$. Compared with these two Si$_{1-x}$Ge$_x$ alloys, there are no pits with a depth above 10 nm for the Si0.06Ge0.94 alloy. In addition, from the $R_q$ (mean square root) roughness, we can find that the surface smoothness of the Si0.06Ge0.94 alloy is the best, and that of the Si0.26Ge0.74 alloy is the worst. In Fig. 5(a) and (b), the mean diameter of pits on the surface is approximately 1.3 μm, so such large and deep surface micro-pits would affect the surface SH signal observably; this point is reflected by the degree of symmetries for the SH vs the rotational angle.

Based on the AFM analysis, we can link the RA-SHG experimental results with the crystal quality of the SiGe alloy. First, the surface roughness generally reduces the p-polarized output, RA-SHG, amplitude and does not affect the s-polarized output, SH [30]. However, for the three SiGe alloy samples with different Ge content, the p-output SH intensity is affected by not only the surface roughness, but also the optical properties of the samples (such as the absorption coefficient and the escape depth of the SH signal from the SiGe alloy). Thus, the SH intensity cannot be directly linked with the surface roughness of the SiGe alloy. Second, a nominally flat, low-Miller-index surface typically has terraces and steps [27]. This is a generic vicinal surface that is misoriented by a small angle from a low-index face to produce a surface with macroscopic C$_{1v}$ symmetry [24]. S. Janz showed that the steps on vicinal surfaces can make significant contributions to the SH response [28] and that the total SH field is the sum of the fields generated by the terraces and by the steps. They showed that the field generated by the steps is proportional to the number of steps [24]. Therefore, the source of the $C^{(1)}$ and $C^{(3)}$ coefficients of RA-SHG originate from step- and terrace-induced plane defects on the surface, respectively. Additionally, the $C^{(1)}$ and $C^{(3)}$ coefficients can be studied via the s-in/s-out polarization combination because this combination contains only anisotropic nonlinear susceptibility tensor elements and is the most sensitive to the in-plane surface symmetry. Different from the vicinal surface, the SiGe alloy surface with pit defects is not flat, and the pit surface is misoriented to a (100) low-index face. Consequently, the pits surface has more complicated terraces and steps. Additionally, the $C^{(1)}$ and $C^{(3)}$ coefficients that are induced by the steps and terraces in the pit defect region will increase with the density of surface pits defects. According to the above theoretic deduction, the degree of eightfold symmetry of the s-in/s-out RA-SHG will decrease with the numbers of surface pit defects in a SiGe alloy, which is consistent with our experimental data.

IV. Conclusions

In conclusion, three strain-relaxed Si$_{1-x}$Ge$_x$ alloys with different Ge components were prepared via UHV-CVD, and the composition $x$ and strain in plane were determined via analysis of the micro-Raman spectra. Although the strain was noticeably relaxed, the residual strain of 0.013~0.015 can induce the enhancement of the p-polarized SH signal, and the strain-induced SH intensity is reflected in the large $C^{(0)}$ of the Fourier coefficients. As a result, the bulk quadruple is dominant for the s-in/s-out SH signal for all three SiGe alloy samples. A common ground for the s-in/p-out and s-in/ s-out SH vs the rotational angle is that the degree of fourfold (the former) and eightfold (the latter) symmetry reduced with the increase of the density of surface pit defects and surface roughness in the Si$_{1-x}$Ge$_x$ alloys, as confirmed by AFM measurements.

REFERENCES


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