Strained and strain-relaxed epitaxial $Ge_{1-x}Sn_x$ alloys on Si(100) substrates*

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Epitaxial $Ge_{1-x}Sn_x$ alloys are grown separately on a Ge-buffer/Si(100) substrate and directly on a Si(100) substrate by molecular beam epitaxy (MBE) at low temperature. In the case of the Ge buffer/Si(100) substrate, a high crystalline quality strained $Ge_{0.97}Sn_{0.03}$ alloy is grown, with a $\chi_{\min}$ value of 6.7% measured by channeling and random Rutherford backscattering spectrometry (RBS), and a surface root-mean-square (RMS) roughness of 1.568 nm obtained by atomic force microscopy (AFM). In the case of the Si(100) substrate, strain-relaxed $Ge_{0.97}Sn_{0.03}$ alloys are epitaxially grown at 150 °C–300 °C, with the degree of strain relaxation being more than 96%. The X-ray diffraction (XRD) and AFM measurements demonstrate that the alloys each have a good crystalline quality and a relatively flat surface. The predominant defects accommodating the large misfit are Lomer edge dislocations at the interface, which are parallel to the interface plane and should not degrade electrical properties and device performance.

Keywords: GeSn alloys, strained, strain-relaxed, molecular beam epitaxy

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1. Introduction

$Ge_{1-x}Sn_x$ alloys have attracted considerable attention due to their potential applications in developing totally group-IV based optoelectronic material systems.[1,2] The band gap of $Ge_{1-x}Sn_x$ has been reported to transform from indirect to direct when the x value is more than 0.1,[3] as the Γ-point conduction band minimum decreases more rapidly than the L-point valleys. In addition, $Ge_{1-x}Sn_x$ alloys also have some potential applications, even though their Sn concentrations are very low, due to the much higher absorption coefficient than that of Ge at a critical wavelength of 1.55 μm.[2,4,5]

Although the growth of $Ge_{1-x}Sn_x$ is complicated by a limited bulk solid solubility, $x < 0.005$, and a trend towards Sn surface segregation, nonequilibrium growth, such as molecular beam epitaxy (MBE) and chemical vapour deposition (CVD), can yield a supersaturated solid solution and suppress Sn surface segregation.[6−11] Previously, $Ge_{1-x}Sn_x$ alloys were always grown on Ge(100) or GaAs(100) substrates[8−11] but monolithic integration with Si(100) is becoming more attractive.

In this paper, we focus on MBE growth of strained $Ge_{1-x}Sn_x$ on a Ge-buffer/Si(100) substrate and strain-relaxed $Ge_{1-x}Sn_x$ directly on a Si(100) substrate at low temperatures. A good Ge buffer provides a much smaller lattice mismatch, on which strained $Ge_{1-x}Sn_x$ alloy is grown with a high crystalline quality. At the same time, epitaxial $Ge_{1-x}Sn_x$ alloys are grown directly on Si(100) substrates. The large lattice mismatch between $Ge_{1-x}Sn_x$ and Si(100) ($> 4.2\%$) makes the films relaxed after growing several monolayers. These results indicate that it is possible to grow epitaxial $Ge_{1-x}Sn_x$ layers directly on Si(100) substrates by MBE, which is achieved only by UHV/CVD with a special gas source[6,7] to our knowledge.

2. Experiment

A cold wall UHV/CVD system equipped with Knudsen cells was used for $Ge_{1-x}Sn_x$ growth on Si substrate. The base pressure was 3.0×10^{-8} Pa. Pure GeH_4 was used for the Ge buffer growth and high pu-

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rity (99.9999%) Ge and Sn solid sources were used for $Ge_{1-x}Sn_x$ deposition. The substrates were 4-inch n-type Si(100) wafers with resistivity in a range of 2 $\Omega\cdot$cm–4 $\Omega\cdot$cm. After RCA cleaning, the wafers were degassed at 400 °C in a pre-treatment chamber for more than 12 h and then baked at 930 °C in a growth chamber for 10 min to deoxidize them. Epitaxial strain-relaxed $Ge_{1-x}Sn_x$ layers were synthesized on Si(100) substrates by MBE in a substrate temperature range of 100 °C–300 °C, while the strained $Ge_{1-x}Sn_x$ layer was grown on a Ge buffer/Si(100) at 150 °C. The thicknesses of the $Ge_{1-x}Sn_x$ layers were all around 230 nm and the Sn compositions of the $Ge_{1-x}Sn_x$ samples were all ∼3%, as measured by Rutherford backscattering spectrometry (RBS). The heteroepitaxy of the Ge buffer on the Si substrate was deposited by a two-step method. An approximately 70-nm thick Ge layer was deposited first at 340 °Cand then the substrate temperature was heated up to 630 °C to grow the main Ge film (∼380 nm). RBS, double-crystal X-ray diffraction (DCXRD), transmission electron microscopy (TEM) and atomic force microscopy (AFM) were used to characterize the crystalline quality, residual strain and surface structure of the layers.

3. Results and discussion

3.1. Growth of strained GeSn on Si(100) with a Ge buffer

The Ge buffer is grown on a Si substrate by following a two-step method, with a surface root-mean-square (RMS) roughness of 0.52 nm and a threading dislocation density of $\sim 1\times10^6$ cm^{-2}. The growth process of the $Ge_{0.97}Sn_{0.03}$ layer is monitored by *in situ* reflection high energy electron diffraction (RHEED) measurement, which indicates that the $Ge_{0.97}Sn_{0.03}$ film is epitaxial and flat at the atomic level, corroborated by postgrowth atomic force microscopy over a 5 μm × 5 μm area of the surface that indicates an RMS roughness of 1.568 nm. The crystalline quality of the $Ge_{0.97}Sn_{0.03}$ alloy and the Sn substitutionalities are evaluated by RBS random and aligned spectra and XRD scans. Deriving the channeling and random RBS spectra (Fig. 1), the values of $\chi_{\min}$ are both 6.7% for Ge and Sn in the $Ge_{0.97}Sn_{0.03}$ sample, indicating that the Sn content is entirely substitutional. A representative X-ray 2θ–ω scan around the (004) reflection shows that the line shape of the $Ge_{0.97}Sn_{0.03}$ peak is very symmetrical (Fig. 2) and the full width at half maximum (FWHM) of the $Ge_{0.97}Sn_{0.03}$ peak and the Ge peak are 0.136° and 0.133°, respectively, indicating a good crystalline quality. Combined with the angular displacement of the $Ge_{0.97}Sn_{0.03}$ (224) asymmetric reflection, the in-plane crystal lattice parameter ($a_{\|}$) is calculated to be 5.6617 Å (1 Å = 0.1 nm), which is very close to $a_{\rm Ge}$ and the degree of strain relaxation is small. The primary mechanism for relieving strain during growth of heteroepitaxial layers lies in the formation of misfit dislocations and strain-induced surface roughening, both of which, however, should be strongly inhibited during low-temperature growth of $Ge_{1-x}Sn_x$ on a Ge substrate.

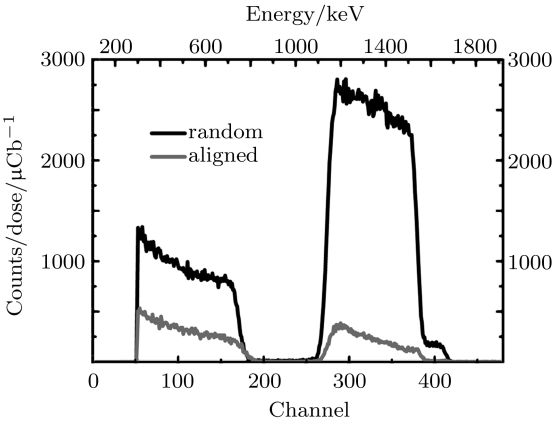


Fig. 1. RBS aligned and random spectra of $Ge_{0.97}Sn_{0.03}$/Ge/Si(100) with good crystallinity.

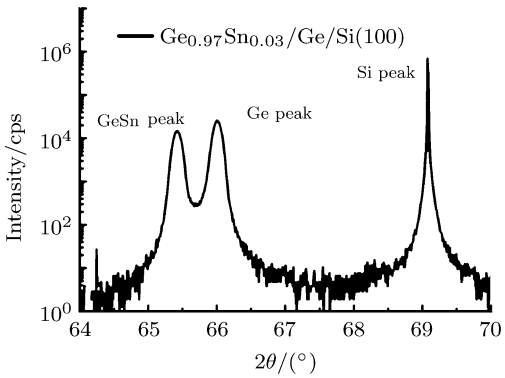


Fig. 2. High resolution 2θ–ω X-ray diffraction profile around the (004) order of the $Ge_{0.97}Sn_{0.03}$/Ge/Si(100) alloy.

3.2. Growth of relaxed GeSn directly on a Si(100) substrate

It is challenging to grow $Ge_{1-x}Sn_x$ alloy directly on a Si(100) substrate because of the large lattice mismatch between $Ge_{1-x}Sn_x$ and Si(100). Takeuchi *et al.*[12] have reported the growth of $Ge_{0.98}Sn_{0.02}$ alloys on a Si(100) substrate, Ge buffer and Ge(100) substrate. They found that the $Ge_{0.98}Sn_{0.02}$ film grown on a Si(100) substrate would turn into to amorphous

phase. Half of the Sn atoms were not incorporated into the lattice site of the $Ge_{0.98}Sn_{0.02}$ crystal, but segregated into the amorphous phase instead. In our experiment, $Ge_{0.97}Sn_{0.03}$ alloys are grown at different temperatures. The growth process is monitored by *in situ* RHEED, which shows that all of the samples remained epitaxial throughout the growth process, except for the one grown at 100 °C. The XRD measurements show the same results (Fig. 3). For the sample grown at 100 °C, there is no obvious $Ge_{0.97}Sn_{0.03}$ peak, which means that there was a transition to an amorphous phase (also confirmed by RAMAN measurements, see Fig. 5). However, for the samples grown at higher temperatures, there are strong and symmetric $Ge_{0.97}Sn_{0.03}$ peaks. The position of the $Ge_{0.97}Sn_{0.03}$ peak does not change and the FWHMs of the $Ge_{0.97}Sn_{0.03}$ peaks decrease with growth temperature increasing, which implies a gradually improved crystalline quality. For the sample grown at 300 °C, the FWHM dropped down to 0.137°. However, the $Ge_{0.97}Sn_{0.03}$ peak shifts toward the right side and becomes asymmetric. There is an obvious shoulder besides the $Ge_{0.97}Sn_{0.03}$ main peak, which may be due to the surface segregation of Sn. To check whether the Sn segregation is driven by the large lattice mismatch between $Ge_{0.97}Sn_{0.03}$ and Si(100), a sample is grown by a two-step method: a ∼170-nm relaxed $Ge_{0.97}Sn_{0.03}$ layer (confirmed by XRD) is grown at 200 °C, and then a ∼70-nm $Ge_{0.97}Sn_{0.03}$ layer is grown on this "lattice match" buffer at 300 °C. The XRD curves (Fig. 4) show that there are two GeSn peaks, one for the buffer layer grown at 200 °Cand the other for the layer grown at 300 °C. For the sample grown at 300 °C, part of the Sn atoms are not incorporated into the lattice site and segregated to the surface, even on the "lattice match" buffer. Thus growth temperature is the key factor for the epitaxial growth of GeSn alloys, rather than the strain.

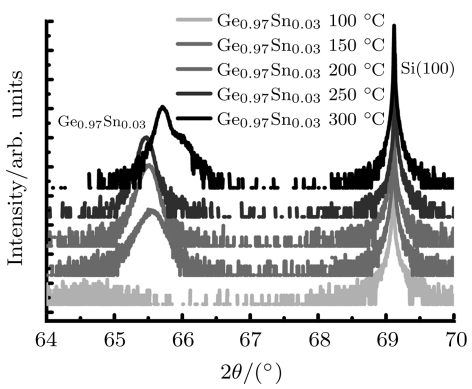


Fig. 3. High resolution 2θ–ω X-ray diffraction profiles around the (004) order of the $Ge_{1-x}Sn_x$ /Si(100) alloys grown at different temperatures.

Cubic lattice parameters for the $Ge_{0.97}Sn_{0.03}$ alloys are inferred from the symmetric (004) and asymmetric (224) reflections. The in-plane ($a_{\parallel}$) and the out-of-plane ($a_{\perp}$) lattice parameter are 5.6804 Å and 5.6945 Å, respectively, for the sample grown at 200 °C. The degree of strain relaxation is as high as 96.9% within experimental resolution. According to Vegard's law, which assumes linear interpolation between the unit cell parameter of Ge and α–Sn, the Sn concentration in the $Ge_{0.97}Sn_{0.3}$ layer on the Si(100) substrate can be estimated to be 3.7% by XRD, which is a little larger than the result by RBS, and this may be attributed to the deviation from Vegard's law.[13]

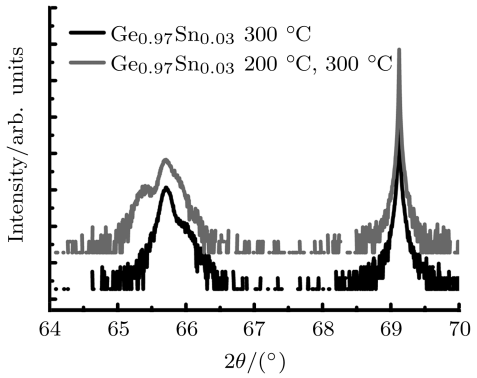


Fig. 4. High resolution 2θ–ω X-ray diffraction of the $Ge_{1-x}Sn_x$ /Si(100) alloys by the two-step method.

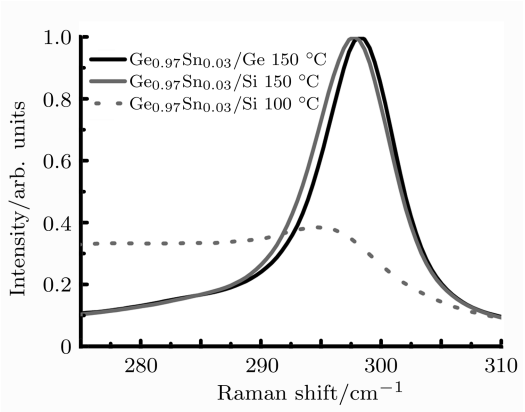


Fig. 5. Raman spectra from $Ge_{0.97}Sn_{0.03}$/Ge/Si(100) and $Ge_{0.97}Sn_{0.03}$/Si(100) grown at 150 °C and $Ge_{0.97}Sn_{0.03}$/Si(100) grown at 100 °C.

The Raman spectra measured with the 488-nm laser line are shown in Fig. 5. However, in our films with high Ge concentrations, we see only unambiguous evidence for the Ge–Ge peak. There is no obvious peak for the sample grown at 100 °C on the Si(100) substrate, while for the sample grown on Ge buffer/Si(100) and Si(100) substrate at 150 °C, the Ge–Ge peaks are located at 298.189 cm^{-1} and

297.76 cm^{-1}, separately. The Raman frequency shift peak in a group-IV alloy can be understood as the sum of two terms, with respect to the value for bulk Ge, $\omega_{\rm Ge} = 301.0$ cm^{-1}: the LO phonon shift in $Ge_{1-x}Sn_x$ due to substitutional-Sn-induced bond stretching in fully relaxed alloys (toward lower energies) and the contribution of compressive strain to the frequency shift (toward higher energies). In our experiment, all the Ge–Ge peaks shift towards lower energies, but the peak of $Ge_{0.97}Sn_{0.03}$ on a Ge buffer shifts less due to the compressive strain in the film.

Figure 6 shows a high-resolution TEM micrograph of the surface morphology (upper panel) and an interface region between $Ge_{0.97}Sn_{0.03}$ and Si(100) (bottom panel). The arrows indicate the locations of misfit dislocations. Almost all the misfit dislocations are located above the $Ge_{0.97}Sn_{0.03}$/Si interface, and the spacing between the misfit dislocations is not strictly constant. For a complete $Ge_{0.97}Sn_{0.03}$ relaxation, the misfit dislocations should be separated by 22.5 Si(111) planes, with spacing of 8.6 nm in the [110] direction. Since the XRD measurements give 56804 Å for $a_{\|}$ measured at 20 °C, the spacing between consecutive dislocations should be equal to 22.8 Si(111) planes, a distance of 8.7 nm along the [110] direction. In this study, the distance is found to be equal to (9.5±0.5) nm, which is a little larger than the value found from the XRD evaluations of $a_{\|}$ measured at 20 °C. This demonstrates that the relaxation process stems mainly (but not only) from the emission of misfit dislocations.

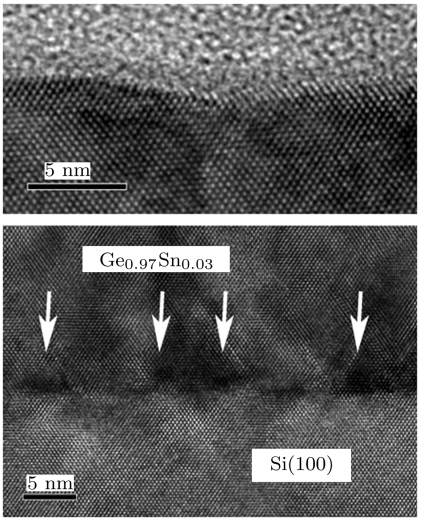


Fig. 6. The cross-sectional electron micrographs of $Ge_{0.97}Sn_{0.03}$ grown at 200 °C. The top panel shows surface morphology of the film. The bottom panel is a high-resolution electron micrograph of the interface region between $Ge_{0.97}Sn_{0.03}$/Si(100) and Si(100). Arrows indicate the location of misfit dislocations.

Figure 7 shows the AFM images of the $Ge_{0.97}Sn_{0.03}$ layers grown at (a) 250 °C and (b) 300 °C, while figure 8 exhibits the evolution of FWHM (from XRD) and surface RMS roughness (from AFM) with growth temperature. During low temperature epitaxy, the surface roughness will increase with film thickness increasing. At some point, the growth front breaks down, resulting in an irreversible transition to amorphous layer growth.[14,15] For the sample grown at 100 °C, the transition has already happened, after which the surface RMS roughness begins to decrease. While for the sample grown at 150 °C, no transition appears, thus the RMS roughness reaches 4.276 nm.

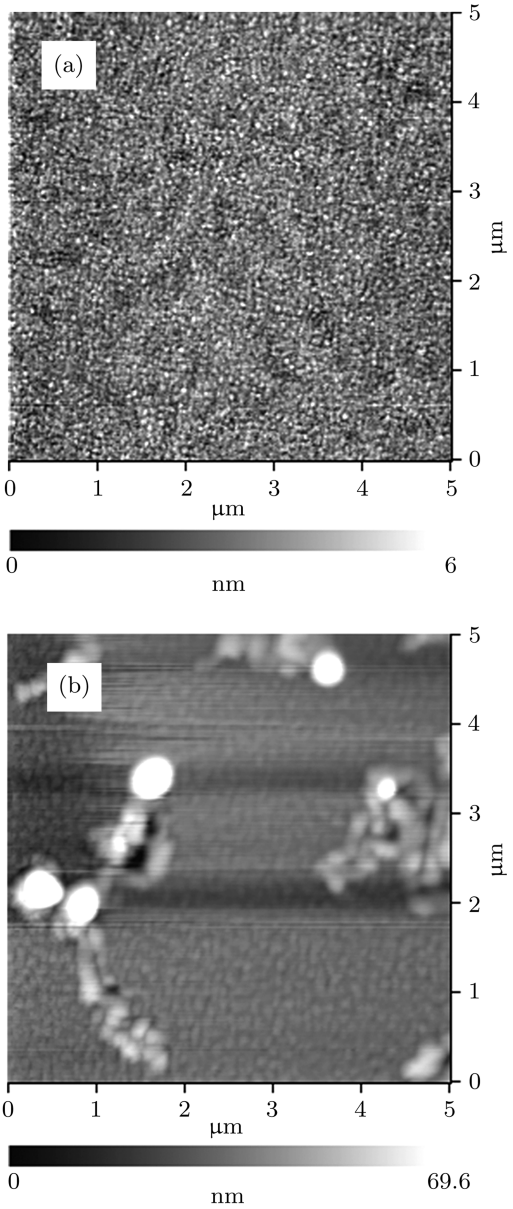


Fig. 7. The AFM images of $Ge_{0.97}Sn_{0.03}$/Si(100) samples grown at (a) 250 °C and (b) 300 °C.

With a higher growth temperature, the RMS roughness begins to decrease. For the sample grown at 250 °C, the RMS roughness drops down to 0.928 nm. However, with a further increase of growth temperature, Sn segregates to the surface (Fig. 7) and the RMS increases abruptly up to 10.63 nm. The challenges to the growing of epitaxial $Ge_{1-x}Sn_x$/Si heterostructures without Sn segregation argue for low temperature deposition in a highly kinetically constrained regime. Unfortunately, lower growth temperatures typically result in a more rapid surface roughening rate, which slowly leads to epitaxial breakdown. Thus the range of growth temperature for epitaxial $Ge_{1-x}Sn_x$ alloys should be very narrow.

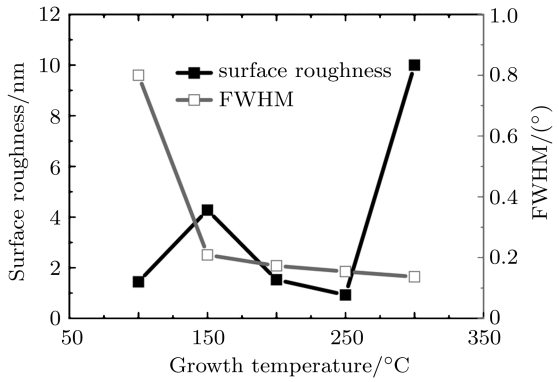


Fig. 8. Evolution of FWHM (from XRD) and surface RMS roughness (from AFM) with growth temperature.

4. Thermal stabilities of the $Ge_{0.97}Sn_{0.03}$ alloys

Some samples are annealed at 500 °C in N_2 atmosphere to determine their thermal stability. The XRD scans are measured and compared with the pre-annealed samples grown on a Ge buffer and a Si(100) substrate. After annealing, the $Ge_{0.97}Sn_{0.03}$ peaks are still strong and sharp, and the line shapes of the peaks remain symmetrical, which indicates that the $Ge_{0.97}Sn_{0.03}$ alloys are highly thermal stable and provides potential applications in optoelectronic device.

5. Conclusions

High crystalline quality $Ge_{0.97}Sn_{0.03}$ alloy is grown on a Ge buffer/Si(100), with a $\chi_{\min}$ value of 6.7% (from RBS) and an FWHM of 0.136° (from XRD). The Ge buffer provides a small lattice mismatch and XRD measurements demonstrate that the film is highly strained. Epitaxial $Ge_{0.97}Sn_{0.03}$ alloys are grown directly on Si(100) substrates in a narrow growth temperature range. The XRD measurements demonstrate that the films are almost completely relaxed, with an FWHM (from XRD) of ∼0.173° and RMS roughness (from AFM) of ∼1.528 nm. The post growth annealing shows that all of the samples are stable up to at least 500 °C.

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