Epitaxial growth of $Ge_{1-x}Sn_x$ films with x up to 0.14 grown on Ge (00l) at low temperature*

Tao Ping(陶 平)[a], Huang Lei(黄 磊)[a], Cheng H H[b], Wang Huan-Hua(王焕华)[c], and Wu Xiao-Shan(吴小山)[a]†

[a] *Laboratory of Solid State Microstructures, Nanjing University, Nanjing* 210093, *China*
[b] *National Taiwan University, Center for Condensed Matter Sciences, Taipei* 106, *Taiwan, China*
[c] *Beijing Synchrotron Radiation Facility (BSRF), Institute of High Energy Physics, Beijing* 100049, *China*

(Received 9 November 2013; revised manuscript received 9 March 2014; published online 20 June 2014)

We characterize the structures of $Ge_{1-x}Sn_x$ films with x up to 0.14 grown on Ge (00l) by molecular-beam epitaxy at low temperature. The results show that $Ge_{1-x}Sn_x$ films are fully strained even at high Sn composition. The in-plane lattice parameters remain exactly the same as that of the substrate. Depth sensitivity analysis of the lattice parameters indicates that the strains of the epitaxial films are all in homogeneity. The films are fully strained. Poisson ratios, the force constants for the bonds between Ge and Sn are estimated and discussed in the present paper. Raman results show Ge–Ge, Ge–Sn, Sn–Sn vibrational modes. The Sn–Sn bond aggregation may respond to the high quality of our films. The fully strained epitaxy films with high content of Sn may be useful in designing the high quality GeSn films.

Keywords: GeSn films, high resolution X-ray diffraction, fully-strained, Raman measurements

PACS: 81.15.–z, 81.15.Hi, 68.55.–a, 68.55.ag **DOI:** 10.1088/1674-1056/23/8/088112

1. Introduction

Sn–Ge solid solution (alloy) has been proved to be a direct band semiconductor with Sn composition higher than 9%. The $Ge_{1-x}Sn_x$ alloys have fantastic optical and electrical properties,[1] which are of potential in the applications of Si-based optoelectronic devices[2] and light emitting devices.[3] The properties of the devices are influenced greatly by the quality of the films.[4]

However, the large lattice mismatch of about 14.7% between Ge and Sn becomes an obstruction in growing high quality epitaxial films. The low equilibrium solubility of Sn in Ge (< 0.01) restricts the formation of $Ge_{1-x}Sn_x$ alloys.[5] Also, growth temperature is critical when we obtain certain samples by molecular beam epitaxy.[6] It is difficult to grow the $Ge_{1-x}Sn_x$ alloys at high or low temperatures.[7–10] At high temperatures, Sn tends to surface aggregate during growth of the $Ge_{1-x}Sn_x$ alloys by molecular-beam epitaxy. At lower temperatures $Ge_{1-x}Sn_x$ alloys tend to roughen the surface.[10] It is, therefore, hard to grow high quality $Ge_{1-x}Sn_x$ films for device applications although high quality films may bring nice optoelectronic properties. In the present paper, the strain structures of the epitaxial $Ge_{1-x}Sn_x$ films are studied by high resolution X-ray diffraction (HRXRD) and Raman measurements. Fully strained films are confirmed by a multiple X-ray diffraction technique. Raman measurements are used to investigate the epitaxial structures of $Ge_{1-x}Sn_x$ alloys.

2. Experimental procedures

High quality $Ge_{1-x}Sn_x$ films are grown on the Ge (00l) substrate by molecular beam epitaxy at the Center for Condensed Matter Science and Graduate Institute of Electronics Engineering, National Taiwan University. Briefly, raw materials, including Ge and Sn, are evaporated through an effusion cell during the deposition. The substrate is n-type Ge (001) with a resistivity of $\sim 0.02\ \Omega$·cm, which is cleaned using standard processing to remove the oxide layer at the surface before film growth.[11] Ge serves as the buffer layer before a 300-Å $Ge_{1-x}Sn_x$ film growth. The growth temperature is kept at 200 °C.

Three composite $Ge_{1-x}Sn_x$ films with the nominal value $x = 0.04$, 0.08, and 0.14 are obtained. The composition of Sn in each $Ge_{1-x}Sn_x$ film can be estimated by X-ray reflectivity measurements, and energy dispersive X-ray spectroscopy (EDX) measurements.[11] The strain, strain-depth distribution, and Poisson ratio are analyzed by HRXRD studies, which can reveal the microstructures of thin films.[12–14] HRXRD experiments are performed on the beamline BL14B1 located at Shanghai Synchrotron Radiation Facility (SSRF). The wavelength of the X-ray is chosen to be 1.238 Å. To confirm the experimental results, similar experiments are also performed at the beamline 1W1B located in Beijing Synchrotron Radiation Facility (BSRF), the wavelength of the X-ray is chosen to be 1.54 Å.

*Project supported by the National Natural Science Foundation of China (Grant Nos. 11274153, 11204124, and 51202108) and the National Key Projects for Basic Research of China (Grant No. 2010CB923404).

†Corresponding author. E-mail: xswu@nju.edu.cn

© 2014 Chinese Physical Society and IOP Publishing Ltd

3. Results and discussion

The quality of the epitaxial films is confirmed from the phi-scan X-ray diffraction with the asymmetric GeSn/Ge reflection of (115). Figure 1 shows the typical phi-scan X-ray diffraction patterns for the sample with $x = 0.14$ with the X ray wavelength of 1.238 Å. Reflections from Ge (115) and GeSn (115) are fully overlapped and separated in 90° each. The full width at half maximum (FWHM) of each of the four reflections is about 2°. And the four reflections are in symmetry, which indicates that the film is well crystallized.

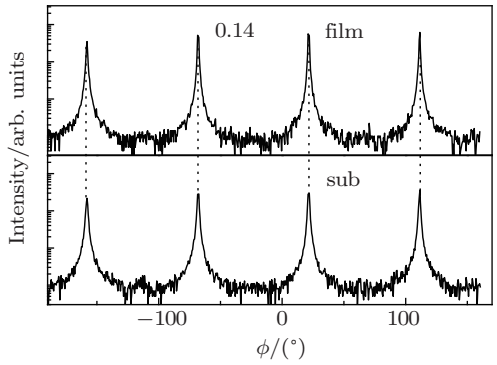


Fig. 1. X-ray diffraction patterns for $x = 0.14$, which are in phi-scan mode around (115) reflection.

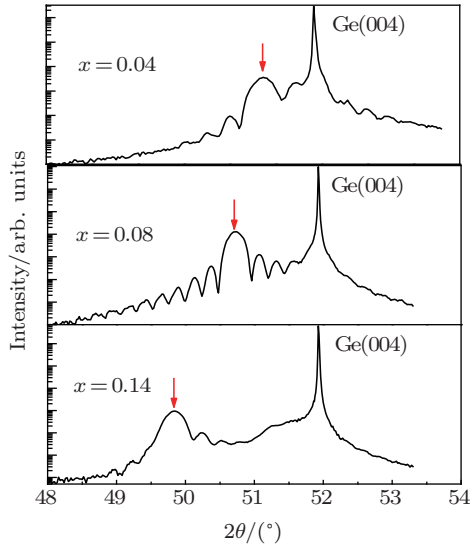


Fig. 2. (color online) High resolution X-ray diffraction patterns for $Ge_{1-x}Sn_x$ with $x = 0.04$, 0.08, and 0.14 are shown.

Figure 2 shows the high resolution X-ray diffraction (HRXRD) patterns for the three samples. Two main reflections, which are from the substrate and the $Ge_{1-x}Sn_x$ films, are observed in the HRXRD patterns. The right peak originates from the substrate, and the left peak, marked by arrows, results from the X-ray diffraction of $Ge_{1-x}Sn_x$ film. With increasing the Sn content, reflections from the $Ge_{1-x}Sn_x$ film shift toward the left, which means that the perpendicular lattice constant (the out-of plane lattice parameter, c) increases with increasing the Sn content. Furthermore, we measure the (115) asymmetric X-ray diffraction ($\theta/2\theta$ connecting scan), together with the asymmetric rocking curves (θ scan). The in-plane lattice constants and out-of-plane lattice constants then can be deduced from the asymmetric and symmetric HRXRD, which is shown in Fig. 3. The in-plane lattice constants are almost the same as that of the substrate Ge, the out-of-plane constants increase with the increase of the Sn content. The results confirm that the $Ge_{1-x}Sn_x$ displays a tetragonal distortion. The full relax $Ge_{1-x}Sn_x$ bulk crystallizes in cubic, and the lattice parameters of the alloys may be deduced based on the Vegard law.[15,16] Figure 3 compares the lattice parameters obtained by Vegard law and those obtained in our experiments.

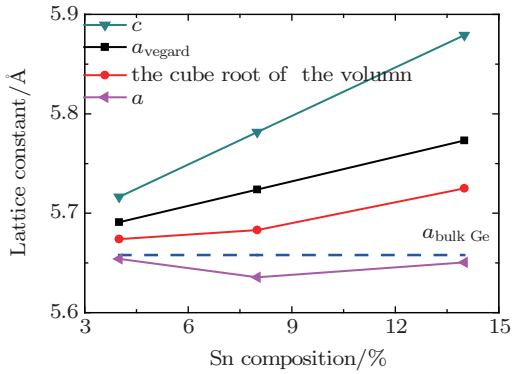


Fig. 3. (color online) The Sn content dependence of the in-plane and the out-of-plane lattice constants for the epitaxy films. The lattice constant of the substrate is indicated by the dashed line. From bottom to top, the solid lines are shown as: in-plane lattice constant of a, the cube root of the unit cell volume, lattice constant deduced by the Vegard rule, and out of-plane lattice constant of c.

We note that the difference between the cube root of the unit cell volume, i.e., $a_{\text{av}} = (a^2 \cdot c)^{1/3}$, and the lattice constant from the Vegard law, a_{Vegard}, $\Delta = a_{\text{Vegard}} - a_{\text{av}}$, increases with increasing the Sn content. Our experiments show that all $Ge_{1-x}Sn_x$ films are in full compressive strain (totally epitaxy). The strain energies in the epitaxial films may increase with increasing the Sn content at the same thickness. When the strain energy is larger enough, the dislocation may form and induce the lattice relax. There is a critical thickness with dislocation free, which may be calculated from the mismatch between the film and the substrate.[17,18] The critical thickness of the $Ge_{0.86}Sn_{0.14}$ film is about 1 nm, which is reported in our previous work.[11] In our case the $Ge_{1-x}Sn_x$ films are fully strained and the films are in epitaxy. Based on the elastic theory, the in-plane compression may induce the out-of plane expansion. The Poisson ratio may indicate the relationship between the in-plane and out-of-plane strain. The Poisson ratio for the epitaxial $Ge_{1-x}Sn_x$ film can be deduced from the strain (ε) in a three-dimensional system. The in-plane strain (ε_{11}, ε_{22}) and out-of-plane strain (ε_{33}) are calculated from the formula $(a - a_{\text{GeSn}})/a_{\text{GeSn}}$. Here, a is the lattice constant of the film obtained from HRXRD and a_{GeSn} is the lattice constant of

GeSn alloy in full relax (bulk), which may be estimated from the Vegard law. The Sn composition is determined by EDX. Then the Poisson ratio for $Ge_{1-x}Sn_x$ film can be calculated based on the following formula:[19]

$$\gamma = \frac{\varepsilon_{33}}{\varepsilon_{33} - \varepsilon_{11} - \varepsilon_{22}}.$$

Figure 4 shows the Poisson ratio dependence of the Sn content. The Poisson ratio increases with increasing Sn content in $Ge_{1-x}Sn_x$. The Poisson ratios of bulk Ge and Sn are respectively 0.25 and 0.36. The Poisson ratio of the $Ge_{1-x}Sn_x$ alloy is between the Poisson ratios of the two end members, i.e., Ge and Sn.

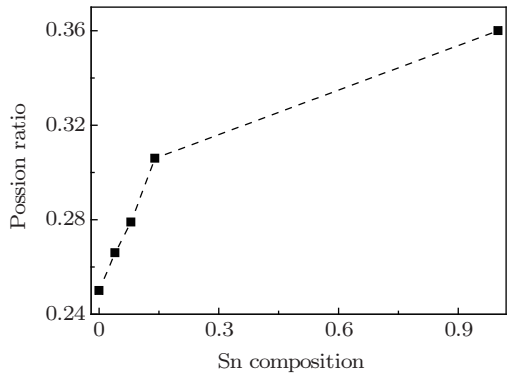


Fig. 4. Variation of Poisson ratio with Sn composition.

Glancing incidence X-ray diffraction (GIXRD) is adopted to study the depth dependence of the strain structure in the $Ge_{1-x}Sn_x$ alloy.[20,21] The wavelength of the X-ray is 1.54 Å. Further depth-sensitive GIXRD[20] proves the previous results. Figure 5 shows the depth dependences of in-plane lattice parameter for the three samples by measuring the (400) reflections of the films with varying the grazing incident angle. All the in-plane lattice parameters remain 5.65 Å, consistent with that of the substrate, which is independent of the film depth. The result indicates that the whole films are in compressive strain, and the growth is epitaxial. This result is the same as that deduced from the X-ray symmetric and asymmetric diffraction.

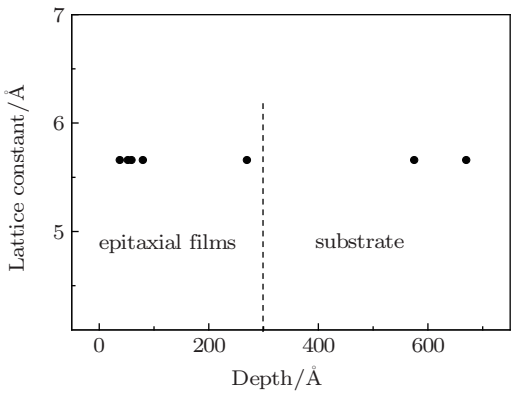


Fig. 5. In-plane constants of three samples remain the same as those of the substrate with increasing depth.

To further understand the above results, we may see the force constants of the bonded Ge–Ge, Ge–Sn, and Sn–Sn. The force constants of Ge–Ge (0.86 N·cm^{-1}), Ge–Sn (0.77 N·cm^{-1}), and Sn–Sn (0.65 N·cm^{-1}) are not the same.[22] The force constant of the Ge–Ge bond is respectively 12% and 32% larger than those of the Ge–Sn and Sn–Sn. Therefore, Ge may be easier to bond with Sn, and Sn is easier to bond with Sn during bonding, which may form the aggregation in the bond area. Figure 6 shows the scheme of the bonding. The bond force constants may help us to understand the fully compressive strained structures of $Ge_{1-x}Sn_x$ alloy films with high Sn content. At the same time, the smallest force constant may bring the Sn–Sn bond during the growth, which can be proved by Raman measurements.

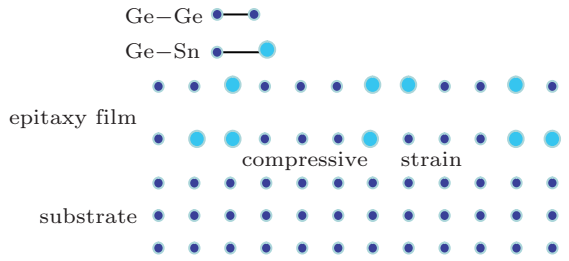


Fig. 6. (color online) Scheme of the process of the growth for GeSn alloys on Ge substrate.

The structures of $Ge_{1-x}Sn_x$ films can be further investigated by Raman spectra, which is a useful method to analyze the structures of thin films.[23,24] Raman scattering spectra are measured by an excitation wavelength of 633 nm at room temperature. The laser intensity is about 1 mW. Figure 7 shows the Raman results of the samples. Various peaks can be obtained by Lorentzian fitting. The left peak indicated by the arrow is about 187 cm^{-1}, which is identified to be due to the Sn–Sn vibration.[25] The existence of Sn–Sn bonds proves our previous results obtained by analyzing force constants and these bonds are critical for growing epitaxial GeSn films. At the same time, the peaks obtained from the other vibrating modes are observed. The peak at 261 cm^{-1} is from the Ge–Sn bond.[26] The Ge–Ge peak at 300.5 cm^{-1}[25] mainly comes from the substrate. From the relative intensity of the peak, the peak at about 285 cm^{-1} may come from Ge–Ge vibration (mainly originating from the Ge–Ge mode in the GeSn layer), which is induced by the tensile strain of the Ge–Ge bond in the film out of plane. Strain in sample can induce the shift of the peaks.[27] Red shift of Raman peaks are always induced by tensile strain.[28] The tensile strain from the bonds of Ge–Ge out of plane can be seen from the lattice constant out of plane in Fig. 3. The Ge–Ge peaks in plane and out of plane confirm the tetragonal distortion structure of the three samples, which are deduced by HRXRD.

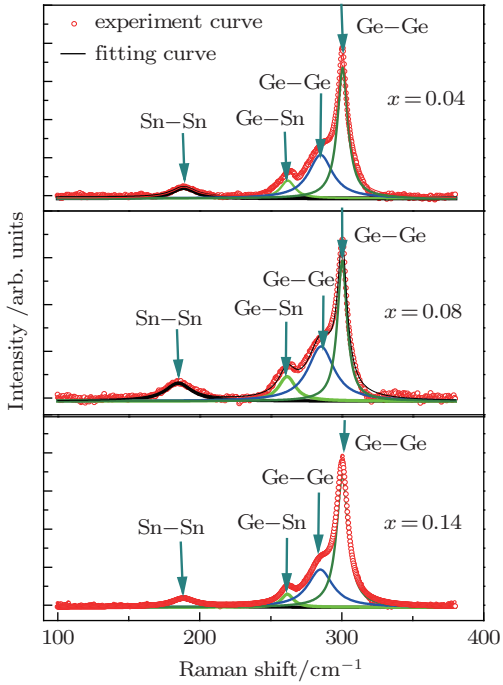


Fig. 7. (color online) Raman spectra for $Ge_{1-x}Sn_x$ films with different quantities of Sn.

Moreover, for samples with different quantities of Sn, the same vibration modes have almost the same peak positions, indicating that $Ge_{1-x}Sn_x$ films have the same strained structure and are all epitaxial films on substrate Ge.

4. Conclusion

Epitaxial $Ge_{1-x}Sn_x$ films are analyzed by a multiple high resolution X-ray diffraction technique. The in-plane lattice parameters are the same as that of the substrate. Depth sensitive lattice parameter analysis shows that the strain of the epitaxial film is in homogeneity. The Poisson ratios of the samples are respectively 0.265, 0.278, and 0.306, for $x = 0.04$, 0.08, and 0.14, which are in the range of the Poisson ratios of the end-member Ge and Sn single crystals. The Sn–Sn aggregation bonding is analyzed by variation of the force constants of the Ge–Ge, the Ge–Sn, and the Sn–Sn bonds, and also the Raman measurements. Raman measurements clearly show the different Ge–Ge bonds in the films.

Acknowledgment

The authors thank beamline BL14B1 (Shanghai Synchrotron Radiation Facility) and BSRF (Beijing Synchrotron Radiation Facility) for providing the beam time.

References

[1] Pe'rez Ladro'n de Guevara H, Rodriguez A G, Navarro-Contreras H and Vidal M A 2003 *Appl. Phys. Lett.* **83** 4942
[2] Su S J, Wang W, Zhang G Z, Hu W X, Bai A Q, Xue C L, Zuo Y H, Cheng B W and Wang Q M 2011 *Acta Phys. Sin.* **60** 028101 (in Chinese)
[3] Nakamura Yoshiaki, Masada Akiko, lchikawa Masakazu 2007 *Appl. Phys. Lett.* **91** 013109
[4] Xing Y H, Han J, Deng J, Li J J and Shen G D 2009 *Acta Phys. Sin.* **58** 2644 (in Chinese)
[5] Rojas-Lopez M, Navarro-Contreras H, Desjardins P, Gurdal O, Taylor N, Carlsson J R A and Greene J E 1998 *J. Appl. Phys.* **84** 2219
[6] Si J X, Wu H Z, Xu T N, Cao C F and Huang Z C 2005 *Chin. Phys. Lett.* **22** 2353
[7] Bratland K A, Foo Y L, Spila T, Seo H S, Haasch R T, Desjardins P and Greene J E 2005 *J. Appl. Phys.* **97** 044904
[8] Bauer M, Taraci J, Tolle J, Chizmeshya A V G, Zollner S, Smith David J, Menendez J, Hu Changwu and Kouvetakis J 2002 *Appl. Phys. Lett.* **81** 2992
[9] Taylor M E, He G, Atwater Harry A and Polman A 1996 *J. Appl. Phys.* **80** 4384
[10] Gurdal O, Desjardins P, Carlsson J R A and Taylor N, Radamson H H, Sundgren J E and Greene J E 1998 *J. Appl. Phys.* **83** 162
[11] Yu I S, Wu T H, Wu K Y, Cheng H H, Mashanov V I, Nikiforov A I, Pchelyakov O P and Wu X S 2011 *AIP Advances* **1** 042118
[12] Xue S W, Zu X T, Shao L X, Yuan Z L, Xiang X and Deng H 2008 *Chin. Phys. B* **17** 2240
[13] Zhong W W, Liu F M, Cai L G, Zhou C C, Ding P and Zhang H 2010 *Chin. Phys. B* **19** 107306
[14] Liao Y P, Shao X B, Gao F L, Luo W S, Wu Y, Fu G Z, Jing H and Ma K 2006 *Chin. Phys.* **15** 1310
[15] Chroneos A, Jiang C, Grimes R W, Schwingenschlogl U and Bracht H 2009 *Appl. Phys. Lett.* **94** 252104
[16] Kasper E, Schuh A, Bauer G, Hollander B and Kibbel H 1995 *J. Cryst. Growth* **157** 68
[17] Hull R, Bean J C, Peticolas L and Bahnck D 1991 *Appl. Phys. Lett.* **59** 964
[18] Shaleev M V, Novikov A V, Yurasov D V, Hartmann J M, Kuznetsov O A, Lobanov D N and KrasilniK Z F 2012 *Appl. Phys. Lett.* **101** 151601
[19] Bharathan Jayesh, Narayan Jagdish, Rozgonyi George and Bulman Gary E 2013 *J. Electron. Mater.* **42** 40
[20] Zhai Z Y, Wu X S, Jiang Z S, Hao J H, Gao J, Cai Y F and Pan Y G 2006 *Appl. Phys. Lett.* **89** 262902
[21] Zhai Z Y, Wu X S, Cai H L, Lu X M, Hao J H, Gao J, Tan W S, Jia Q J, Wang H H and Wang Y Z 2009 *J. Phys. D: Appl. Phys.* **42** 105307
[22] Ormeci Alim, Aydemir Umut and Somer Mehmet 2011 *Z. Anorg. Allg. Chem.* **637** 907
[23] Zheng W T and Sundgren J E 1998 *Chin. Phys. Lett.* **15** 120
[24] Li X, Tang Z A, Ma G J, Wu Z M and Deng X L 2003 *Chin. Phys. Lett.* **20** 692
[25] Stefanov S, Conde J C, Benedetti A, Serra C, Werner J, Oehme M, Schulze J, Buca D, Hollander B, Mantl S and Chiussi S 2012 *Appl. Phys. Lett.* **100** 104101
[26] Oehme M, Schmid M, Kaschel M, Gollhofer M, Widmann D, Kasper E and Schulze J 2012 *Appl. Phys. Lett.* **101** 141110
[27] Su S J, Wei W, Cheng B W, Hu W X, Zhang G Z, Xue C L, Zuo Y H and Wang Q M 2011 *Solid State Commun.* **151** 647
[28] Kil Y H, Yang H D, Yang J H, Kim J H, Jung J Y, Kang S, Jeong T S, Kim T S and Shim K H 2013 *J. Korean Phys. Soc.* **63** 1034