Applied Surface Science 256 (2010) 3299–3302

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Effect of strain relaxation of oxidation-treated SiGe epitaxial thin films and its nanomechanical characteristics

Bo-Ching He [a], Hua-Chiang Wen [b,*], Tun-Yuan Chinag [b], Zue-Chin Chang [b], Derming Lian [b], Wei-Hung Yau [b], Wen-Fa Wu [c], Chang-Pin Chou [a]

[a] *Department of Mechanical Engineering, National Chiao Tung University, Hsinchu 300, Taiwan*
[b] *Department of Mechanical Engineering, Chin-Yi University of Technology, Taichung 411, Taiwan*
[c] *National Nano Device Laboratories, Hsinchu 300, Taiwan*

ARTICLE INFO

Article history:
Received 22 October 2009
Received in revised form 22 November 2009
Accepted 7 December 2009
Available online 16 December 2009

PACS:
61.72.uf
61.05.cp
81.16.Ta
62.20.Qp

Keywords:
Silicon–germanium
X-ray diffraction
Atomic force microscope
Hardness

ABSTRACT

In this study, we examined the effect of high-temperature oxidation treatment on the SiGe epitaxial thin films deposited on Si substrates. The X-ray diffraction (XRD), atomic force microscopy (AFM), and nanoindentation techniques were employed to investigate the crystallographic structure, surface roughness, and hardness (*H*) of the SiGe thin films, respectively. The high-temperature oxidation treatment led to Ge pileup at the surface of the SiGe thin films. In addition, strain relaxation occurred through the propagation of misfit dislocations and could be observed through the cross-hatch pattern (800–900 °C) and SiGe islands (1000 °C) at the surface of the SiGe thin films. Subsequent hardness (*H*) measurement on the SiGe thin films by continuous penetration depth method indicated that the phenomenon of Ge pileup caused a slightly reduced *H* (below 50 nm penetration depth), while relaxation-induced defects caused an enhanced *H* (above 50 nm penetration depth). This reveals the influence of composition and defects on the structure strength of high-temperature oxidation-treated SiGe thin films.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Many investigations on the field of SiGe thin films have been executed in recent years because, due to the lattice misfit between Si and Ge atoms [1–3], SiGe thin films on Si substrate can provide a suitable site for the growth of tensile-strained Si overlayer. In this overlayer, the carrier mobility has direct proportion to the degree of strain, that is to say, high Ge content of strain-relaxed SiGe thin films can serve as "virtual substrate" and is efficient for higher device performance of MOSFET and/or photodetectors [4,5].

The conventional method for obtaining high Ge content of strain-relaxed SiGe virtual substrate is to fabricate compositionally graded films, which possess low density of threading dislocations [6–8]. However, long time consuming in the fabrication process due to films thickness in the micrometer range and low thermal conductivity-induced self-heating effect would cause higher cost and lower thermal impedance [9]. Another pathway toward the formation of the virtual substrate is high-temperature treatment-induced strain relaxation in inert gases or vacuum environment. During this process, the SiGe thin films could relax if the thermal budget is enough to overcome the relative activation barrier. Besides, the required thickness of the SiGe thin films is only located at the metastable range and is thinner than that of graded one. Nevertheless, this method accompanies with interdiffusion at SiGe/Si interface, which would decrease the Ge content and then degrade the performance. Therefore, both these two methods have a serious bottleneck for throughput.

Recently, high-temperature oxidation treatment on the SiGe thin films offers a suitable manner for virtual substrate. There are several reports on the mechanisms and kinetics of this oxidation process. Yin et al. [10] utilized dry oxidation to increase Ge content and found that the strain relaxation was carried out in the form of SiGe islands instead of dislocations. Cai et al. [9] also used dry oxidation method on strained SiGe thin films and found that the surface roughness and the threading dislocation densities are kept low during the whole oxidation processes. Zhang et al. [11] proposed that the competition between Ge accumulation and diffusion led to different strain relaxation

* Corresponding author. Tel.: +886 423924505-6703; fax: +886 423930681.
E-mail address: a091316104@gmail.com (H.-C. Wen).

0169-4332/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2009.12.022

behaviors by wet oxidation. In brief, Ge atoms not only accumulate at the surface of SiGe thin films because of selective formation of SiO_2 but also diffuse toward substrate due to high-temperature treatment, which results in compositionally grade effect [9]. Therefore, it offers an effective manner to form an ideal virtual substrate.

Consequently, this reveals the variation of strain and distribution of Ge content in the SiGe thin films after high-temperature treatment. However, it usually accompanies with generation of defects and inhomogeneous composition in the thin films, which would lead to varied structure strength. The stress generated during device manufacturing process would cause damage to heterostructure and then degrade device performance. Therefore, it requires better understanding of mechanical characteristics in order to evaluate the yield reliability and device performance [12,13].

The crystal structure, surface morphology, and nanomechanical characters of the SiGe thin films during oxidation treatment at different temperatures have been studied in this article. The result shows that not only high Ge content and strain relaxation were formed but also relative varied structure strength was revealed through Berkovich-induced deformation of the SiGe thin films.

2. Experimental procedure

The samples used in this study were prepared by a standard Radio Corporation of American (RCA) clean and a HF:H_2O (1:50) bath for 15 s. p-Type Si(1 0 0) wafers were introduced into load-lock chamber of ultra-high vacuum chemical vapor deposition (UHV/CVD) system. The expected thin films were obtained according to the following three steps: (i) A 5-nm-thick Si buffer layer was deposited on the Si substrate at 500 °C for 15 min from pure SiH_4 (in 100 sccm) gas. (ii) A 200-nm-thick $Si_{0.8}Ge_{0.2}$ thin films was deposited at 500 °C from pure SiH_4 (in 100 sccm) and GeH_4 (in 10 sccm) gases and the vacuum was achieved at 10^{-7} mbar. (iii) In the oxidation process, the SiGe thin films are endured thermal treatment at different temperatures (800, 900, and 1000 °C) for 30 min *ex situ* in furnace in atmosphere environment.

The crystal structures of as-deposited and oxidation-treated SiGe thin films were measured by X-ray diffraction (XRD, PANalytical X′Pert Pro Inc. Singapore, with Cu K_α; λ = 0.154 nm). 3D surface morphology of the SiGe thin films was observed by atomic force microscope (AFM, Veeco D5000) in tapping mode after the top oxide removed by buffered oxide etchant (BOE). Besides, AFM can measure surface roughness in the form of root-mean-square (R_{ms}).

The subsequent hardness (H) of the SiGe thin films was measured by using a Nano Indenter XP instrument (MTS operation, Nano Instruments Innovation Center, TN, USA). The instrument was calibrated by using a standard fused silica sample prior to the beginning of indentation. A diamond Berkovich indenter tip (tip radius ~50 nm) was used in the nanoindentation measurements, which suggests that plastic deformation can be generated at very small load. H, the resistance to local plastic deformation, can be determined by using the Oliver and Pharr analysis [14] and has been conventionally obtained by measuring the load (P) and the projected contact area (A_c):

$$H = \frac{P}{A_c} \tag{1}$$

A_c and contact depth h_c have relation $A_c = 24.56h_c^2$ [15]. Continuous contact stiffness measurement (CSM) mode, which was executed by superimposing small oscillations on the force signal to record stiffness data along with load and displacement data dynamically, is useful to obtain the continuous variation of H relative to penetrating displacement. Therefore, H can be calculated at every data point acquired during the indentation experiment. After that, ten indents were made on samples to minimize the deviation of the results. Besides, the nanoindentations were sufficiently spaced (50 μm) to prevent from mutual interactions. Before the beginning of each indentation, the drift rate was preset to <0.05 nm/s.

3. Results and discussion

The XRD rocking curve is useful for analyzing the quality of epitaxial thin films. Fig. 1 exhibits the XRD spectra of the (0 0 4) rocking curves for (a) as-deposited sample and oxidation-treated samples at (b) 800, (b) 900, and (c) 1000 °C, respectively. From as-deposited sample, the two peaks at the position of 69.126 and 67.906 are silicon substrate and the SiGe thin films, respectively. The obvious oscillation characteristic of the curve, which is called thickness fringes, means that the atoms are arranged in an ordered form. It also suggests that the as-deposited sample exhibits good crystal quality [16]. Besides, the composition and thickness of the SiGe thin films can be calculated from the fringes [17]. Hence, the ratio of Si to Ge (4:1) and the thickness of 200 nm are confirmed, indicating that the SiGe thin films are in a metastable state and kept in full strained. The angular separation between Si and SiGe peaks decreases with increasing oxidation temperature. It is suggested that strain relaxation occurred and the Ge mole fraction decreases due to interdiffusion at SiGe/Si interface [18]. Moreover, the fade out of the fringes can be attributed to strain relaxation and interdiffusion-induced broadened interface. Compared to original SiGe peak, there are new small broad peaks appeared at lower angles in curves of oxidation-treated samples. It has the similar tendency to that described by Ref. [19]. This phenomenon was due to Ge pileup at the surface of SiGe during oxidation effect [20] and therefore the phase of SiGe containing high Ge content was observed.

In order to obtain ideal device performance, high degree of strain relaxation, low root-mean-square (R_{ms}) roughness, and reasonably low level of surface defect density of the SiGe thin films are required [21]. Fig. 2 shows AFM measurement of 3D surface morphology. The as-deposited sample (Fig. 2(a)) exhibits flat surface (R_{ms} is 0.5 nm) and almost no surface

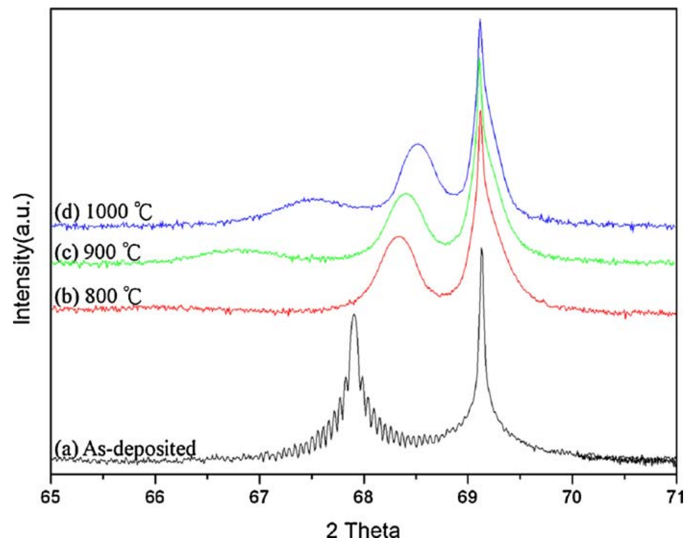

Fig. 1. The XRD rocking curve for 200 nm of the SiGe thin films deposited on Si substrates at various oxidation temperatures: (a) no oxidation, (b) 800 °C for 0.5 h, (c) 900 °C for 0.5 h, and (c) 1000 °C for 0.5 h.

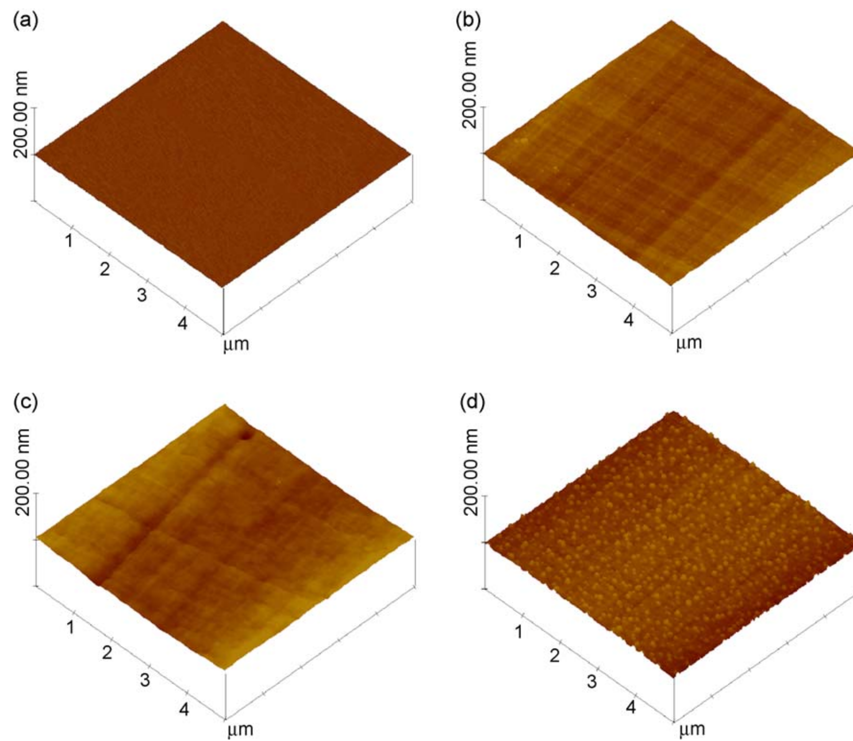

Fig. 2. AFM images of surface topography of samples at various oxidation temperatures: (a) no oxidation, (b) 800 °C for 0.5 h, (c) 900 °C for 0.5 h, and (c) 1000 °C for 0.5 h.

defects appearing on it. While the SiGe thin films endured oxidation treatment at 800 and 900 °C for 30 min, cross-hatch pattern emerged from the surface (Fig. 2(b) and (c)), indicating that strain relaxation occurred. Cross-hatch pattern is known to be caused by misfit dislocations traveling at SiGe/Si interface [22]. In addition, Chen et al. [23] suggested that cross-hatching is not related to composition fluctuation regardless of the stress undulation associated with strain relaxation in the SiGe thin films. The cross-hatch morphology arises from vertical lattice relaxation induced by piled-up misfit dislocations in the SiGe buffer layer and substrate. Due to the generation of cross-hatch pattern, the R_{ms} of oxidation-treated samples at 800 and 900 °C are 1.2 and 2.5 nm and are slightly higher than that of as-deposited one. The surface morphology has different variation while 1000 °C oxidation treatment for 30 min was carried out (Fig. 2(d)). Except for above mentioned phenomenon, a dense network of SiGe islands populated the surface and relative R_{ms} is 2.1 nm. Tételin et al. [24] pointed out that strain relaxation leads to formation of islands on the SiGe strain thin films surface while oxidation temperature is above 900 °C. They also demonstrated that these 3D islands are because of the fact that Ge segregated on the surface of SiGe thin films and this phenomenon conforms to XRD analysis in our study. Besides, the nucleation of islands was driven by misfit-dislocation strain. There are almost no etch pits observed from all the AFM morphologies of treated samples, implying that fewer threading dislocations occurred during high-temperature oxidation treatment [25]. From above observation, we suggest that the strain relaxation occurred in the form of generating misfit dislocations and islands, which leads few increase in R_{ms}.

Nanoindentation technique is powerful in probing the deformation behaviors of thin films. In this experiment, the SiGe/Si heterostructures with/without oxidation treatments were investigated from continuous penetration depth by means of CSM in nano-size. Fig. 3 shows the H of the SiGe/Si heterostructures as functions of the indentation at 200 nm, following the method proposed by Oliver and Pharr [14]. The hardness increases with the indentation depth up to 25 nm, which can be attributed to the transition between purely elastic to elastoplastic contact whereby the hardness is actually the contact pressure. Comparing with as-deposited sample, the lower H measured from oxidation-treated ones at depths below 50 nm may be caused by the Ge pileup at the surface of SiGe. Tsui et al. [26] demonstrated that since the force of the indenter is compressive and acts perpendicularly to the surface, compressive strain should increase the H by diminishing the shear stresses beneath the indenter. In this case, oxidation treatment-induced high Ge content would easily lead to strain relaxation. In other words, compressive strain decreases rapidly at surface of the SiGe thin films and therefore

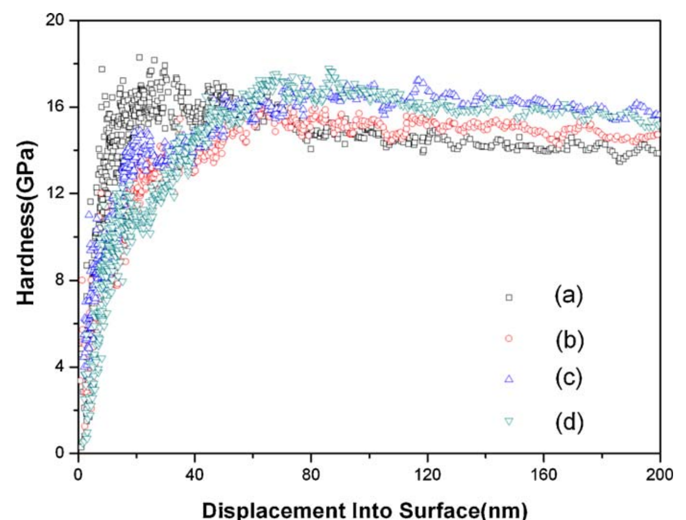

Fig. 3. The H of the SiGe thin films samples at various oxidation temperatures: (a) no oxidation, (b) 800 °C for 0.5 h, (c) 900 °C for 0.5 h, and (c) 1000 °C for 0.5 h.

the H became lower compared with as-deposited one. In addition, Ge is softer than Si, which leads to an unstable microstructure. The H became constant after indentation depth exceeding 25 nm. Therefore, the average H was determined by averaging measurements at indentation depths from 100 to 200 nm, considering the adequate depth to achieve a fully developed plastic zone. Following the above method, the average H are 14.5 ± 0.6, 15.0 ± 0.6, 16.1 ± 0.4, and 16.2 ± 0.5 GPa for as-deposited sample and samples oxidized at 800, 900, and 1000 °C, respectively. The result shows that the strength of SiGe/Si heterostructure can be enhanced through oxidation treatment. Ref. [27] has the similar trend and shows that dislocations occurred in the SiGe thin films accompany with the enhancement in mechanical resistance against elastic and elastoplastic deformations. Consequently, we suggest that high-temperature oxidation treatment leads to strain relaxation in the form of misfit dislocations, which can increase hardness. The effect of defects and composition of the SiGe thin films on H was revealed.

4. Conclusions

The XRD, AFM, and nanoindentation techniques have been used to investigate the crystalline nature, surface features, and nanomechanical properties of the SiGe thin films with high-temperature oxidation treatment.

From the XRD analysis, not only strain relaxation but also Ge pileup at the surface of SiGe thin films occurred while the oxidation treatment was executed. Besides, strain relaxation can be reflected on the misfit dislocations-induced cross-hatch pattern (800–900 °C) and SiGe islands (1000 °C) which result from Ge segregation at the surface. It is obviously observed that the smooth manner (R_{ms} is 0.5 nm) gradually roughens from 800 to 1000 °C (R_{ms} are from 1.2 to 2.1 nm). Results from nanoindentation exhibited that below the indentation depths of 50 nm, the H of oxidation-treated samples was lower than that of as-deposited one. This phenomenon was attributed to the condensed Ge on the surface of the SiGe thin films. However, we observe that the misfit-dislocation propagation plays a critical role in H (indentation depths excess 50 nm) of the SiGe/Si heterostructures with high-temperature oxidation treatment. It demonstrates that the reliable mechanical properties as well as surface phenomenon by means of nanoindentation method in the SiGe thin films.

Acknowledgements

This research was supported by the National Science Council in Taiwan under contract NSC 98-2216-E-009-069 and by National Nano Device Laboratories in Taiwan under Contract NDL98-C03SP-128 and NDL98-C03SP-127.

References

[1] M.L. Lee, E.A. Fitzgerald, M.T. Bulsara, M.T. Currie, A. Lochtefeld, J. Appl. Phys. 97 (2005), 011101-1-011101-27.
[2] T. Mizuno, S. Takagi, N. Sugiyama, H. Satake, A. Kurobe, A. Toriumi, IEEE Elect. Dev. Lett. 21 (2000) 230–232.
[3] N. Usami, K. Kutsukake, W. Pan, K. Fujiwara, T. Ujihara, B. Zhang, T. Yokoyama, K. Nakajima, J. Cryst. Growth 275 (2005) e1203–e1207.
[4] F. Schäffler, Semicond. Sci. Technol. 12 (1997) 1515–1549.
[5] L. Colace, G. Masini, G. Assanto, IEEE J. Quantum Electron. 35 (1999) 1843–1852.
[6] E.A. Fitzgerald, Y.-H. Xie, M.L. Green, D. Brasen, A.R. Kortan, J. Michel, Y.-J. Mii, B.E. Weir, Appl. Phys. Lett. 59 (1991) 811–813.
[7] K.K. Linder, F.C. Zhang, J.-S. Rieh, P. Bhattacharya, D. Houghton, Appl. Phys. Lett. 70 (1997) 3224–3226.
[8] V. Terzieva, L. Souriau, F. Clemente, A. Benedetti, M. Caymax, M. Meuris, Mater. Sci. Semicond. Process. 9 (2006) 449–453.
[9] K. Cai, C. Li, Y. Zhang, J. Xu, H. Lai, S. Chen, Appl. Surf. Sci. 254 (2008) 5363–5366.
[10] H. Yin, K.D. Hobart, F.J. Kub, S.R. Shieh, T.S. Duffy, Appl. Phys. Lett. 84 (2004) 3624–3626.
[11] Y. Zhang, K. Cai, C. Li, S. Chen, H. Lai, J. Kang, Appl. Surf. Sci. 255 (2009) 3701–3705.
[12] S.Y. Chang, H.L. Chang, Y.C. Lu, S.M. Jang, S.J. Lin, M.S. Liang, Thin Solid Films 460 (2004) 167–174.
[13] S.Y. Chang, Y.C. Huang, Microelectron. Eng. 84 (2007) 319–327.
[14] W.C. Oliver, G.M. Pharr, J. Mater. Res. 7 (1992) 1564–1583.
[15] J.L. Hay, G.M. Pharr, 10th ed., ASM Handbook: Material Testing and Evaluation, vol. 8, International Materials Park, OH, USA, 2002, pp. 232–242.
[16] G. Bhagavannarayana, P. Zaumseil, J. Appl. Phys. 82 (1997) 1172–1177.
[17] E. Rosendo, A.G. Rodríguez, H. Navarro-Contreras, M.A. Vidal, R. Asomoza, Y. Kudriavtsev, J. Appl. Phys. 89 (2001) 3209–3214.
[18] S. Zheng, M. Kawashima, M. Mori, T. Tambo, C. Tatsuyama, Thin Solid Films 508 (2006) 156–159.
[19] Y.M. Chang, C.L. Dai, T.C. Cheng, C.W. Hsu, Appl. Surf. Sci. 254 (2008) 3105–3109.
[20] Y.S. Lim, J.S. Jeong, J.Y. Lee, H.S. Kim, H.K. Shon, H.K. Kim, D.W. Moon, Appl. Phys. Lett. 79 (2001) 3606–3608.
[21] T.H. Loh, H.S. Nguyen, C.H. Tung, A.D. Trigg, G.Q. Lo, N. Balasubramanian, D.L. Kwong, S. Tripathy, Appl. Phys. Lett. 90 (2007), 092108-1-092108-3.
[22] E.A. Stach, K.W. Schwarz, R. Hull, F.M. Ross, R.M. Tromp, Phys. Rev. Lett. 84 (2000) 947–950.
[23] H. Chen, Y.K. Li, C.S. Peng, H.F. Liu, Y.L. Liu, Q. Huang, J.M. Zhou, Qi-Kun Xue, Phys. Rev. B 65 (2002), 233303-1-233303-4.
[24] C. Tételin, X. Wallart, D. Stiévenard, J.P. Nys, D.J. Gravesteijn, J. Vac. Sci. Technol. B 16 (1998) 137–141.
[25] T. Hino, S. Tomiya, T. Miyajima, K. Yanashima, S. Hashimoto, M. Ikeda, Appl. Phys. Lett. 76 (2000) 3421–3423.
[26] T.Y. Tsui, W.C. Oliver, G.M. Pharr, J. Mater. Res. 11 (1996) 752–759.
[27] B.C. He, C.H. Cheng, H.C. Wen, Y.S. Lai, P.F. Yang, M.H. Lin, W.F. Wu, C.P. Chou, Microelectron. Reliab., in press.