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The influence of the edge effect of the mask on the strain and the morphology of SiGe film grown at the patterned Si substrate by molecular beam epitaxy

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Abstract

The influence of the edge effect of the mask on the strain and the morphology of the $Si_{0.8}Ge_{0.2}$ films grown at the patterned Si substrates with different mask materials were studied. Experiments showed that for the $Si_{0.8}Ge_{0.2}$ films grown in the micron size windows by molecular beam epitaxy, both the strain and the dislocation density would be less than that of the film grown at the large area of the same substrate, as the film thickness was over the critical thickness for pesudomorphic growth. This phenomenon did not conform with the common case that the strain of the heteroepitaxial film would reduce while the misfit dislocation occurred. Further studies on the strain at different regions of $Si_{0.8}Ge_{0.2}$ film in the window were made by micro Raman scattering spectrum measurement. The results showed that if the SiO_2 film was used as the mask material, the strain of the $Si_{0.8}Ge_{0.2}$ film at the margin of the window was larger than that of the film at the central area. But the contrary case could be observed if the mask material of Si_3N_4 was used. Besides the obvious differences of the morphology of the $Si_{0.8}Ge_{0.2}$ films in the windows with different mask materials were observed by atomic force microscope measurements. We suggest that these results may be attributed to the edge effects of the mask and the epitaxial film.

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1. Introduction

As the dimension of the device became smaller and smaller, many authors [1,2] paid much attention to the size effect on the dislocation density and the strain relaxation of the hetero-epitaxial film grown in a finite size window. Nobel et al. [2] and Fitagerald et al. [3] found out that the dislocation density in the SiGe film in the window would decrease as the window size became smaller, and got the linear dependence of the misfit dislocation density upon the window size. Fitagerald et al. [3] concluded that the blocking effect of the dislocation propagation at the edges of the individual structures was the possible explanation for this dependence. The experimental results of Hollander et al. [4] showed that as the window size was reduced, the dislocation density became lower and the strain in SiGe film was consistently increased. These experimental results indicated that for the lattice mismatched heterostructure, the window size would be an important factor for the strain and the dislocation density of the epitaxial film in micron size window. But in these experiments no authors noticed the influence of the mask material on the strain and other properties of the epitaxial films, especially as the window size was in the range of several microns or less. Xiong et al. [5] found out that for a partially relaxed $Si_{0.8}Ge_{0.2}$ film, if the window sizes were less than 20×20 μm^2 the dislocation density would decrease along with the reduction of the window size, and at the same time the strain in the SiGe films in the window would decrease too. This result was contrary to

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the common case that the strain relaxation would become more serious as the dislocation density increases, and meant that other than the misfit dislocation there should be some other causes, which induced the relaxation of the strain. Their experiments also showed that the strain relaxation of the epitaxial SiGe film in the window might also depend upon the mask material of the window. They suggested that these results were possibly due to some edge effects of the epitaxial film and the mask material [5,6]. In this paper we will report the experimental results about the influence of the mask materials on the strain and the morphology of the SiGe films grown in the micron size windows, and will discuss the possible causes for these results.

2. Experimental details

In the experiments p type Si (001) wafers with the resistivity of 20 Ω·cm were used as the substrates of the samples, and two kinds of samples with different mask materials were studied. For sample I the silicon wafer was thermally oxidized at first to grow a layer of SiO_2 at its surface. The substrate was then patterned by photolithography to make the windows of 3×3 μm^2 in the SiO_2 film. In order to make the sidewalls of the windows perpendicular to the substrate, dry etching technique was used to remove the SiO_2 film in the window. At the same time a pretty large area of SiO_2 film about tens of squared millimeters on the substrate was also removed by etching and the surface of the Si substrate was then exposed. Thus the SiGe films on this large area and that in the windows could be epitaxially grown at the same time. For sample II, its configuration was almost the same as sample I except for the mask material of Si_3N_4 film, which was deposited at the surface of the Si substrate by chemical vapor deposition (CVD) technology. Both the film thickness of the SiO_2 and the Si_3N_4 were around 450 nm. Molecular beam epitaxy (MBE) growth of SiGe film was performed in a Riber EVA-32 system. Before epitaxy, the patterned Si substrates of the two samples were chemically cleaned by Shirake process [7]. After loading the substrate into the growth chamber and desorbing the oxide on the silicon substrate surface, a silicon buffer layer and a layer of $Si_{1-x}Ge_x$ film were successively grown with the growth temperature of 600 °C and 550° C, respectively. The evaporation rates of the Ge and the Si sources were controlled by a Sentinel III deposition controller, which was calibrated by measuring the thickness of the film with the X-ray diffraction technology. The thickness of the Si buffer layer was 50 nm, and the Ge atomic fraction x and the film thickness of the $Si_{1-x}Ge_x$ film was 0.2 and 220 nm, respectively.

The strain and the misfit dislocation lines of the $Si_{0.8}Ge_{0.2}$ films were studied at first. The strain of the SiGe films in the windows and that at the large substrate area was measured by X-ray diffraction (XRD) using (400) configuration. The misfit dislocation lines of $Si_{0.8}Ge_{0.2}$ films were revealed by etching with the modified Schimmel solution, which consisted of 55 vol.% CrO_3 (0.4 M) and 45 vol.% HF (49%) [8]. In order to measure the strain of the $Si_{0.8}Ge_{0.2}$ film at different regions in the window, micro Raman scattering spectrum was also made with a machine of Renishaw Raman microscope. Its exciting source was an Ar^+ laser with the wavelength of 514.5 nm, and its space resolution was 1.0 μm. The morphology of the SiGe films was measured using atomic force microscope (AFM) (Solver P47, NT-MDT, Russia) at room temperature and in contact mode with a silicon cantilever.

3. Results and discussion

Since the thickness of the $Si_{0.8}Ge_{0.2}$ films of the two samples was over the critical thickness for pseudomorphic growth [9], the strain of $Si_{0.8}Ge_{0.2}$ films of both samples should be partially relaxed. So the misfit dislocation density in the $Si_{0.8}Ge_{0.2}$ films of the two samples was firstly studied. The dislocation lines of the two samples revealed by etching were shown in Fig. 1. In Fig. 1(a), for the $Si_{0.8}Ge_{0.2}$ film grown at the large area there was a lot of cross-hatched lines in both orthogonal ⟨110⟩ directions, which were related to the misfit dislocations. It meant that the strain of the $Si_{0.8}Ge_{0.2}$ film was really relaxed as expected. But it was interesting to find out that for the $Si_{0.8}Ge_{0.2}$ films in the windows of the two samples, only a very few misfit dislocation lines in some of the windows could be observed, as shown in Fig. 1(b) and (c).

As the misfit dislocation density and the strain relaxation were closely related, the strain of the SiGe films of the two samples was then studied by X-ray diffraction technique. The XRD spectra of the $Si_{0.8}Ge_{0.2}$ films of the two samples were shown in Fig. 2, and the strain got from these spectra was listed in Table 1. It could be seen in this table that for the two samples a similar phenomenon occurred. The strain of the $Si_{0.8}Ge_{0.2}$ films in the windows of 3×3 μm^2 and that of the film at the large area was not same, and the former was less than the latter. It is worth noticing that in common case, as the film thickness is thicker than the critical value, the strain of the SiGe film in the SiGe/Si heterostructure will decrease while the misfit dislocation density becomes higher. But in this experiment, unlike the common case, for the $Si_{0.8}Ge_{0.2}$ film in the window its dislocation line density, as well as its strain, was much less than that of the $Si_{0.8}Ge_{0.2}$ film at the large area. Obviously this result could not be explained simply by the blocking effect of

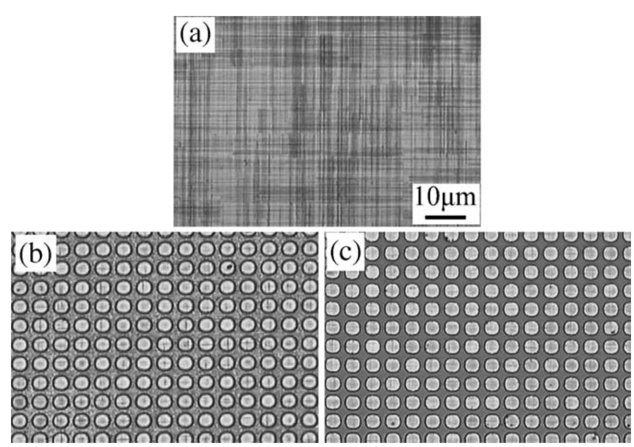

Fig. 1. The misfit dislocation lines of $Si_{0.8}Ge_{0.2}$ films of sample I and sample II. (a) At the large area. (b) In the windows of sample I. (c) In the windows of sample II.

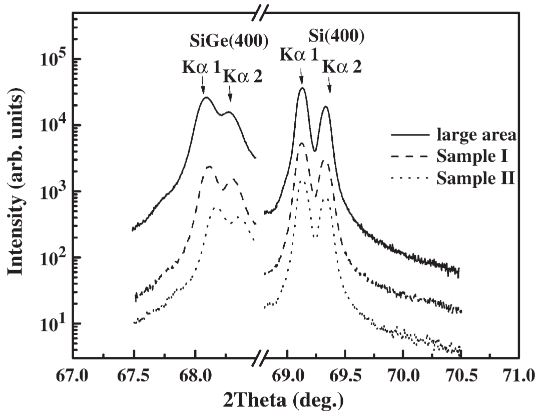

Fig. 2. XRD spectra of $Si_{0.8}Ge_{0.2}$ films grown at the large area and in the windows for sample I and sample II.

the dislocation propagation at the edges of the individual structures suggested by Fitagerald et al. [3]. This experimental phenomenon consisted with the results of Xiong et al. [5], but it showed further that the similar results could be obtained for the $Si_{0.8}Ge_{0.2}$ film in the window with the different mask material of Si_3N_4 (in which there was high tensile stress), and that the strain of the $Si_{0.8}Ge_{0.2}$ film in the window with the Si_3N_4 mask was significantly less than that in the window with the SiO_2 mask.

In order to study the influence of the mask material on the strain of the $Si_{0.8}Ge_{0.2}$ film in the window, Raman scattering spectra of the $Si_{0.8}Ge_{0.2}$ films in the windows at the margin and at the central area were measured by micro Raman scattering spectrum technique. Fig. 3 showed all the spectra of the two samples. In Fig. 3 three peaks located respectively near 288, 408, and 513 cm^{-1} were due to the nearest neighbor Ge–Ge, Si–Ge, and Si–Si atomic vibration of the $Si_{0.8}Ge_{0.2}$ film. The peak located at 520.5 cm^{-1} was due to the Si–Si atomic vibration of the Si substrate, and the peak near 435 cm^{-1} was attributed to the localized Si–Si vibration in the neighborhood of one or more Ge atoms. The phonon frequencies ω_{Si-Si} and ω_{Si-Ge} of the Si–Si and Si–Ge mode of the two samples were listed in Table 2. It was obvious that for each sample there were differences in the phonon frequencies at different places. Since the phonon energies of SiGe film depended on its Ge composition x and the strain, it meant that for the two samples the strain and the Ge composition at the margin and at the center part were not same. For small values of strain the shift of the phonon frequency was linear with the strain

Table 1
The strain of $Si_{0.8}Ge_{0.2}$ films of sample I and sample II from XRD spectra

Sample	Peak position in XRD spectra		Strain $\varepsilon_{/\!/}$
	Si(400)	SiGe(400)	
$Si_{0.8}Ge_{0.2}$ film at large area	69.120	68.079	−6.82E−03
$Si_{0.8}Ge_{0.2}$ film in the window of sample I (SiO_2 mask)	69.120	68.105	−6.23E−03
$Si_{0.8}Ge_{0.2}$ film in the window of sample II (Si_3N_4 mask)	69.120	68.161	−5.26E−03

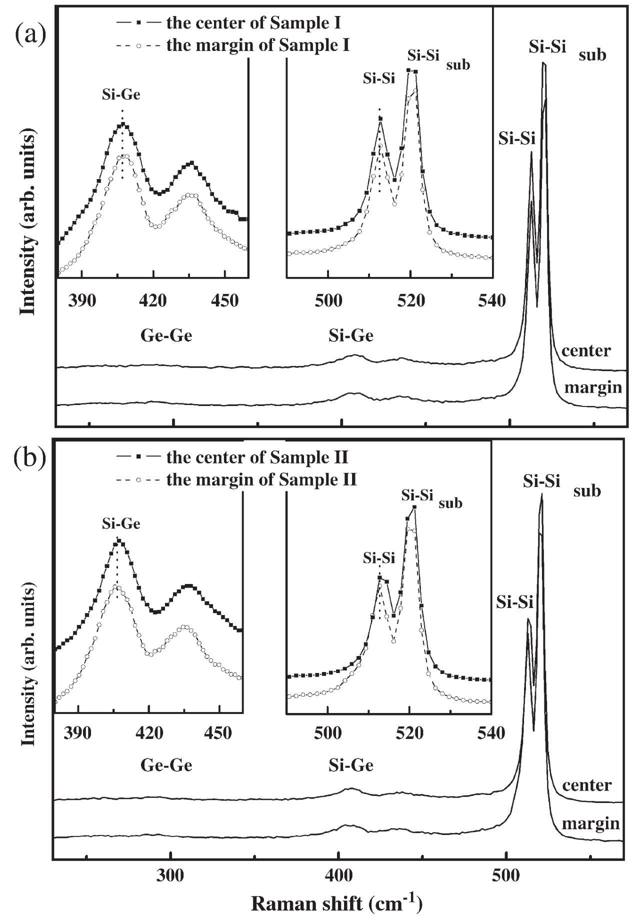

Fig. 3. Raman spectra of $Si_{0.8}Ge_{0.2}$ films in the windows at the margin and the central area for (a) sample I and (b) sample II. The insets are the amplified peaks of Si–Ge and Si–Si mode of the two samples at different regions.

[10,11]. For $x<0.5$, the dependence of the phonon frequencies ω_{Si-Si} and ω_{Si-Ge} on the composition x and the in-plane strain $\varepsilon_{/\!/}$ of $Si_{1-x}Ge_x$ film could be written as:

$$\omega_{Si-Si} = 520.5 - 62x - \Delta_{Si}\varepsilon_{/\!/} \tag{1}$$

$$\omega_{Si-Ge} = 400.5 + 14.2x - \Delta_{GS}\varepsilon_{/\!/} \tag{2}$$

$$\varepsilon_{/\!/} = (a_{/\!/} - a_{Si_{1-x}Ge_x})/a_{Si_{1-x}Ge_x} \tag{3}$$

Here, $\Delta_{Si}=815$ and $\Delta_{GS}=575$ were the strain-shift coefficients for the Si–Si and the Si–Ge mode, $a_{/\!/}$ was the lattice constant of the epitaxial $Si_{1-x}Ge_x$ film parallel to the substrate surface and $a_{Si_{1-x}}Ge_x$ was the lattice constant of the unstrained $Si_{1-x}Ge_x$ film.

The Ge composition x and the strain $\varepsilon_{/\!/}$ at different places of the two samples could be obtained from ω_{Si-Si} and ω_{Si-Ge} with the Eqs. (1) and (2). The data of x and $\varepsilon_{/\!/}$ were listed in the last two columns of Table 2. (It should be pointed out that there was a little discrepancy between the strain got from the XRD measurement and Raman scattering spectra measurement. We

Table 2
The strain $\varepsilon_{//}$ and Ge composition x of SiGe films at different regions in the windows for sample I and sample II from Raman scattering spectra

Samples	Location	Peak position of Raman scattering spectra		Ge composition in $Si_{1-x}Ge_x$	Strain $\varepsilon_{//}$
		ω_{Si-Si}	ω_{Si-Ge}	x	
SiGe in the window	edge	512.8	407.8	0.21	−7.40E−03
Sample I	center	512.6	407.1	0.20	−6.48E−03
(SiO_2 mask)					
SiGe in the window	edge	512.7	406.6	0.19	−5.82E−03
Sample II	center	513.4	407.4	0.20	−7.05E−03
(Si_3N_4 mask)					

x: Ge composition, $\varepsilon_{//}=(a_{//}-a_{Si_{1-x}Ge_x})/a_{Si_{1-x}Ge_x}$.

suggest that this discrepancy may be from the inaccuracy of Δ_{Si} and Δ_{GS}, which was reported as different values by different authors [12]).

In Table 2, it was interesting that for sample I the strain of the $Si_{0.8}Ge_{0.2}$ film in the window at the marginal area was larger than that at the central area, and that the contrary case occurred for the sample II. For these strain differences we will try to explain them by the edge effect of the mask material and the edge induced strain relaxation of the epitaxial film. For sample I the mask material is SiO_2 and there should be compressive stress in the SiO_2 film due to the thermal expansion mismatch between the Si substrate and the SiO_2. Thus the surface atoms of the Si substrate near the edge of the window will move inward due to the stress induced by the edge effect of the SiO_2 mask, and in this way these atoms will be compressed, as illustrated in Fig. 4(a). So the strain of the epitaxial SiGe film grown at the margin of the window will become larger. Besides there is another edge effect which will affect the strain at the margin of the epitaxial film. At the edge of the epitaxial film, the atoms of the film will move outward to relax the strain, and in doing so they drag the lattice planes of the substrate along with them [6], as shown in Fig. 4(c). By this effect the strain at the edge of the epitaxial SiGe film in the window will be relaxed. As a result the strain at the margin of the SiGe film in the window will be affected by the two edge effects described above. Considering the results from the XRD measurements that the strain of $Si_{0.8}Ge_{0.2}$ in the window (which is the average of the strain for the whole window) is less than that at the large area, we can conclude that for sample I the edge induced strain relaxation of the epitaxial film should be the dominant effect. But as the strain at the margin of the SiGe film is larger than that at the central area for sample I, so the edge induced stress by the mask significantly affects the strain of the SiGe film in the window, especially near the edge of the window.

For sample II, the mask material is Si_3N_4, and the strain at the edge of the Si substrate in the window induced by the mask material of Si_3N_4 is tensile (the intrinsic stress of Si_3N_4 grown by CVD is tensile). The lattice constant of the surface atoms at the margin of the Si substrate in the window will become a little larger, as shown in Fig. 4(b). In this case the strain of the epitaxial SiGe film at the margin will become less. As discussed above the edge induced strain relaxation of the epitaxial film will also reduce the strain of the film at the margin, so for sample II the strain at the margin of the SiGe film will be less than that at the center part. These are the possible reasons for the differences between the strain at the margin and at the central area in the SiGe films of the two samples. Besides by the same reason it can be easily understood why in Table 1 the strain of $Si_{0.8}Ge_{0.2}$ film in the window of sample II (with the Si_3N_4 mask) is less than that of sample I (with the SiO_2mask).

Further experiments showed that the mask material would also affect the morphology of the SiGe film in the window. Fig. 5 showed the surface images and the cross-section profiles of the two samples measured with AFM before and after growing the $Si_{0.8}Ge_{0.2}$ films in the windows. In this figure, distinct morphology differences of the $Si_{0.8}Ge_{0.2}$ films in the windows between the two samples could be observed. For sample I, at the marginal area of the SiGe film in the window, a small peak appeared, as shown in the profile of Fig. 5(c) (solid line). It meant that the film thickness near the edge of the window was thicker than that of the other parts of the film. The width of the peak was about several hundreds nanometer and the height was about 20 nm. But for sample II no peaks could be observed, as shown in Fig. 5(d) (solid line), and the SiGe film thickness at the margin was a little thinner than that in the central area. By comparing to the cross section profiles of the substrates in the windows after the surface treatment (the dotted lines in Fig. 5(c) and (d)), it is obvious that the special features of the morphology of the $Si_{0.8}Ge_{0.2}$ films were formed during the growth. For the $Si_{0.8}Ge_{0.2}$ films of the two samples, all of the growth condition,

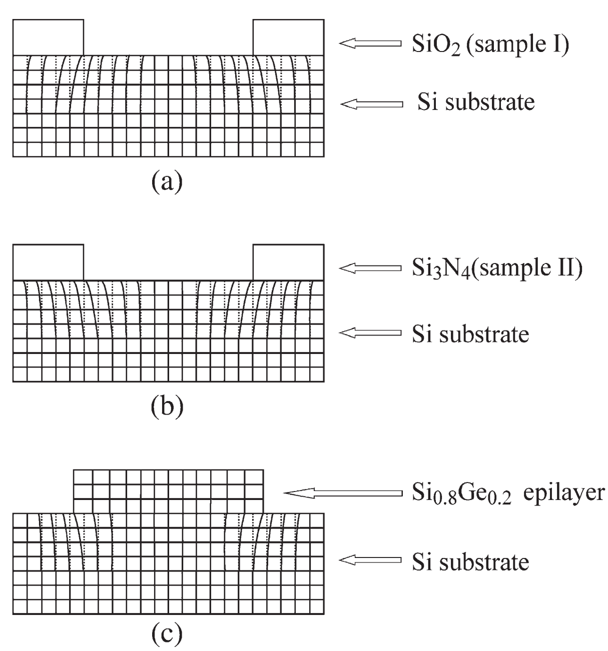

Fig. 4. The schematic diagrams of the edge effect of the mask and the epitaxial film. (a) Strain induced by the edge of the SiO_2 film. (b) Strain induced by the edge of the Si_3N_4 film. (c) Strain relaxation at the edge of the epitaxial SiGe film induced by the edge effect.

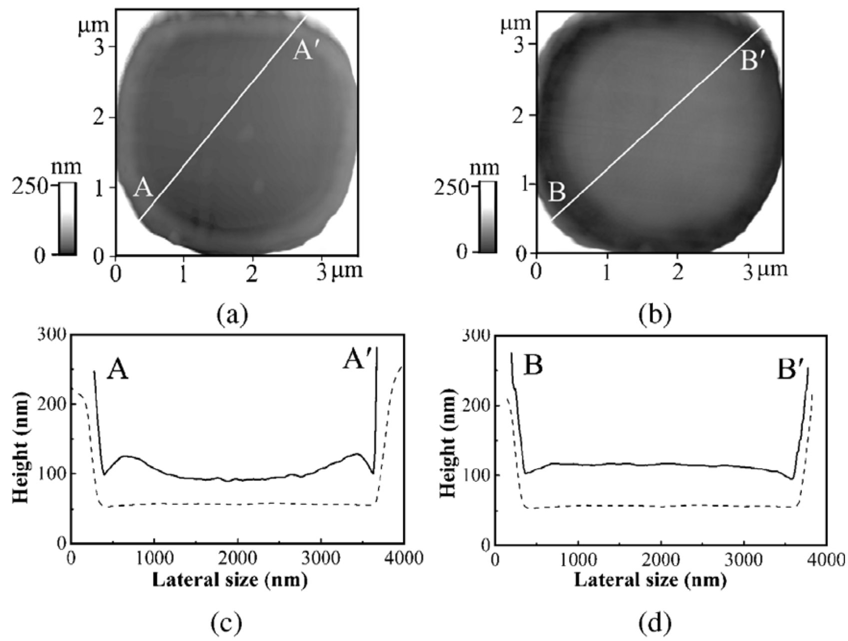

Fig. 5. The AFM images and the cross-sectional profiles of $Si_{0.8}Ge_{0.2}$ films of sample I and sample II. (a) The AFM image of sample I. (b) The AFM image of sample II. (c) The profile of the $Si_{0.8}Ge_{0.2}$ films of sample I (solid line). (d) The profile of the $Si_{0.8}Ge_{0.2}$ film of sample II (solid line). The dotted lines in (c) and (d) are the profiles of the substrates in the windows with the corresponding mask material after surface treatment. The lines A–A′, B–B′ show the places for measuring the cross-section profiles.

the film thickness and the Ge composition x were same, as described above, and the only difference between the two samples was the mask material. So the difference of the surface morphology between the two samples had to originate from the different materials of the masks.

For MBE growth, the surface morphology of the film is governed by the kinetics and the diffusion barrier of the adatoms is one of the important factors for determining the surface morphology of the film. Therefore to discuss the influence of the strain on the diffusion barrier of the adatoms and the strain disribution of the substrate surface are the keys for studying the special features of the film morphology in our experiment. We previously pointed out that the strain at the marginal area of the epitaxial SiGe film in the window is affected by two edge effects, the edge induced stress by the mask material and the edge induced strain relaxation of the epitaxial film. Obviously the influences of these edge effects on the strain of SiGe film will decay along with the increasing of the distance away from the edge of the window, and the strain distribution at the marginal area is determined by the influence of these edge effects. For sample I, the edge induced stress by the SiO_2 mask will increase the strain of the SiGe film at the margin, and the edge induced strain relaxation of the epitaxial SiGe film will reduce it. In this case it is possible that a peak of compressive stress in the epitaxial SiGe film may appear somewhere near the edge of the window. But for sample II, both the edge effects will reduce the strain at the margin of the epitaxial SiGe film, and therefore no peaks of the strain may appear near the margin.

Many authors [13–15] studied the dependence of the strain on the diffusion barrier for the Si and Ge adatoms on the Si substrate. Shu et al. [13] got the linear dependence of the diffusion barrier on the external strain for the Si adatoms on Si (001) substrate in all cases. Zoethout et al. [14] concluded by their experiment that the overall effect of the tensile strain is a decrease in barrier height. From the results of these experimental and theoretical studies, we can come to a conclusion for our experiments that the tensile strain would enhance the diffusion rate, while the compressive strain would lower the rate of diffusion. For sample I, its mask is made of SiO_2, so the adatoms at the margin of the window will diffuse with the lower diffusion rate due to the compressive strain in the substrate. Usually more atoms will accumulate at the region where the adatoms diffusion rate is lower, so a peak will form at the region where the maximum compressive stress exists. As we discussed above, for sample I a peak of compressive strain possibly appears somewhere near the edge of the window, therefore a peak in the morphology may appear at the marginal area of the SiGe film, as shown in Fig. 5(c). For sample II, there is tensile stress at the margin of the Si substrate because of the mask of Si_3N_4. In this case the diffusion rate of the adatoms at the edge of the window will be higher than that at the central area. So it is reasonable that the SiGe film near the edge of the window will be thinner than that at the central area, as shown in Fig. 5(d). These are the possible reasons for the formation of the special features of the morphology for sample I and sample II.

As the morphology of the SiGe film in the window is closely related to the strain, the peak in Fig. 5(c) denotes the area, where the strain of the SiGe film is apparently influenced by the edge effect of the SiO_2 mask. That is, the strain of the SiGe film in the window will be increased at the marginal area of several hundreds of nanometer in width. Therefore if the epitaxial SiGe film is grown in a submicron size window, more obvious influence on the strain of the epitaxial film by the edge effect of the mask will be expected.

4. Conclusion

For the lattice mismatched SiGe/Si heterostructure epitaxialy grown in the micron size window, the strain of the SiGe film in the window is significantly influenced not only by the edge effect of the epitaxial film, but by the edge effect of the mask material. The edge effect of the epitaxial film will induce the strain relaxation of the SiGe film at the marginal area in the window, while the influence by the edge effect of the mask on the strain of the epitaxial film will depend upon the different kinds of stress induced by the mask. The compressive stress at the marginal area of the window induced by the SiO_2 mask will increase the strain of the epitaxial SiGe film, while the tensile stress at the edge of the window induced by the Si_3N_4 mask will reduce its strain. If the strain relaxation of the SiGe film in the window is due to these kinds of edge effects, the misfit dislocation density of the SiGe film may decrease at the same time. Different influences on the morphology of the SiGe films in the windows by the edge effects of the masks of SiO_2 and Si_3N_4 have also been observed. We suggest that the difference of the morphology can possibly be explained by the different strain distribution in the Si substrate in the window and the dependence of the diffusion rate of the adatoms upon the strain.

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