Investigations of morphology and formation mechanism of laser-induced annular/droplet-like structures on SiGe film

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Abstract: We describe the fabrication of nanostructures on SiGe film by KrF excimer laser with nanosecond pulse width, and find a more direct and clear relationship between the laser irradiation conditions and the nanoscale structures. Perfect annular nanostructures around scattering points on the SiGe film are firstly obtained after the irradiation of a KrF excimer pulse laser beam (100 mJ/cm²) at different incident angles. The different shapes of annular structures are related to different energy distributions due to the optical interference between the scattered light and the incident beam. As laser energy increases, a threshold of pulse energy (230 mJ/cm²) is found, above which a droplet-like morphology completely replacing the surface annular structures. And the disorder morphology is mainly caused by the thermal effect of the incident beam.

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1. Introduction

Micro/nanostructure patterning with an ultrashort pulse laser source is a unique technique which can modify the surface morphology of the materials, and it has attracted great research interests in the fields of laser processing, solar cells, optical memories and optoelectronics [1–5]. The formation of parallel grooves on laser-irradiated surfaces was first reported by Birnbaum [6] in 1965. Since then, numerous studies about laser-induced periodic surface structures (LIPSSs) have been investigated on a variety of materials achieved by lasers with nanosecond to femtosecond pulse width and wavelength ranging from ultraviolet to mid-infrared [7–17]. Up to now, although abundant experimental results concerning the LIPSSs on semiconductors and metals have been reported, there is no systematical study on the mechanism of the laser-induced nanostructures. In particular, during the processing of nanosecond laser, the morphology of the nanoscale structures changes significantly under different laser irradiation conditions. A deeper exploration of relevant mechanism is needed to achieve a direct and clear relationship between laser irradiation conditions and the induced nanostructures, for a better control to fabricate desired nanostructure for practical applications.

In this paper, various nanostructures induced by KrF excimer laser on SiGe film are systematically presented. Moreover, we find a more direct and clear relationship between the laser irradiation conditions and the nanoscale structures. The experiments indicate that optical interference would occur on SiGe surface when the size of surface scattering points is similar with the laser wavelength. Furthermore, perfect annular structures around scattering points are obtained with a suitable laser incident angle. Their shapes are in good agreement with the simulated optical fringes due to the interference between the scattered light and the incident beam. And we observe that the laser-patterned nanostructures are sensitive to pulse intensity. As laser pulse energy increases, a droplet-like morphology becomes a dominant feature and completely replaces the surface annular structures when pulse energy exceeds 230 mJ/cm².
2. Experiments

2.1 Materials fabrication

The SiGe film was epitaxially grown on a 4 inch n-type Si (100) wafer with resistivity of 0.1-1Ωcm, using a cold-wall ultrahigh vacuum chemical vapor deposition (UHV/CVD) system under a base pressure of $5 \times 10^{-8}$ Pa. Firstly, the wafers were cleaned by RCA method and dried by N$_2$ before loading into the growth chamber. The wafers were baked at 850 °C for 30 min to de-oxide. Then a 32-nm-thick low temperature Ge (LT-Ge) film was deposited on n-type Si (100) substrate in the system from a solid Ge source. Ge was deposited by thermal evaporation of 99.999% elemental Ge in a Knudsen cell. The evaporation source used was an effusion cell of high temperature which was heated to 1100 °C. The Si substrate temperature was maintained at 180 °C and the sample was rotating during deposition to assure homogeneous coverage. Finally, pure Si$_2$H$_6$ and GeH$_4$ were used as precursors, and the pressure during the growth of material was about $10^{-2}$ Pa. About 170-nm-thick SiGe layer was deposited on the LT-Ge layer at 400-500 °C in the deposition system.

2.2 Laser modification

A KrF excimer laser, which operates at wavelength of 248 nm with 25-ns pulse width and a 5-Hz repetition rate, was used in all experiments carried out herein. A top flat beam profile of 5 mm × 8 mm was obtained to ensure the uniform annealing of samples, and samples were irradiated at different energy densities by using a metallic neutral density filters. All experiments were performed in nitrogen ambient to avoid oxidation, and the morphologies of the formed surface structures were characterized by a scanning electron microscopy system (SEM, LEO 1530, with an operating voltage of 20 kV).

3. Results and discussion

Figures 1(a)-1(b) are SEM images of the as-grown SiGe samples before laser irradiation, where the black points on the surface are threading defects formed during deposition of SiGe film on Si substrate. Figures 1(c)-1(d) show SEM of the SiGe surface morphology after 1500 laser pulses irradiation with an energy density of 100 mJ/cm$^2$, and Figs. 1(e)-1(f) are the close-up images. These figures precisely show two kinds of microstructures achieved in our experiments: (i) uniform and perfect annular structures around surface defects with obvious interference indicated in Figs. 1(c) and 1(e), where the size of the surface defects is similar with the laser wavelength (248 nm). (ii) However, when the size of the surface defects (1 µm) is much larger than the laser wavelength (248 nm) as shown in Figs. 1(d) and 1(f), there are unobvious ripples.

After analyzing these two main microstructures, we conclude that the surface annular structures are related to the size of the surface defects. It is understandable that when their size is same with that of laser wavelength (248 nm), the surface defects can be treated as scattering points and the laser beam presents its wave character. But its wave character will become unobvious because of the large surface defects (1 µm), which ultimately results in the disorder ripple structures on SiGe surface.
For further mechanism analysis of the annular structures, we changed the incident angle of the laser beam in the following experiments. Periodic annular structures are observed, which are induced by laser beam with energy density of 100 mJ/cm², at various incident angles. In the left part of Fig. 3, obviously, the ratio of the forward and backward scattering annular structures depends on the incident angle. The comparison of experimental data and fitting results $\lambda/(1\pm \sin \theta)$ [18,19] are list in Fig. 2. The periodic lengths of backward annular structures correspond exactly to the fitting results when the incident angle is below 45° (45° included). However, when it reaches 60°, they are wholly different from the theoretical predictions, disorder islands become a dominate morphology, and we cannot obtain the experiment data (indicated by × in Fig. 2). At forward position, the fitting curve is in good agreement with the experimental data when the incident angle is below 30° (30° included). Similarly, when the angle is bigger than 30°, they are wholly away from the theoretical curve. As distinctly showed in the experiments, the ripple structures tend to replace perfect annular structures when they are far from the scattering points. The Eq used herein does not take the distribution of the interference field into consideration. We deduce that the surface annular structures are related to the energy distribution of the laser beam on the SiGe surface, and they can be formed only when the incident beam and the scattered light are in the same frequency.

Taking the optical interference into account, the intensity distribution and interference fringes will be determined as long as the wavelength and the angle of the incident laser are established. In our model, firstly, we fix the size of surface defect comparable to the laser wavelength, so the surface defects are recognized as scattering points. Then the incident beam scattered around the scattering points can be seen as spherical wave which propagates radially on SiGe surface. And the complex amplitude of spherical wave is given by Eq. (1). Moreover, a plane wave was chosen for the incident wave, the complex amplitude of which is shown in Eq. (2). Lastly, if there exists only one scattering point on the surface, we calculated the time-averaged interference intensity on SiGe surface with the Eq. (3).
Fig. 2. The comparison of experiments and fitting results is list in this figure. The solid lines represent the fitting lines of the periodic length vs incident angle according to the Eq \( \lambda/(1 \pm \sin(\theta)) \). At the backward position, the annular structures disappear for the case of 60° incident angle, and we use “×” to remark the theoretical result.

\[
U_z(P) = \frac{A_z}{r_z} \exp\left[j\vec{k} \cdot \vec{r}_z\right] \quad (1)
\]

where \( \vec{r}_z \) is the position vector of the spherical wave, \( A_z \) is the amplitude of the spherical wave, and \( \vec{k} \) is the wave vector of the spherical wave, respectively.

\[
U_1(P) = \Lambda_1 \exp\left[jk \cdot \vec{r}_1\right] = \Lambda_1 \exp\left[jk(\cos \alpha + y \cos \alpha)\right] \quad (2)
\]

\( \alpha \) in this Eq is the angle of the incident beam.

\[
U(P) = U_1(P) + U_z(P) = \Lambda_1 \exp\left[jk \cdot \vec{r}_1\right] + \frac{A_z}{r_z} \exp\left[j\vec{k} \cdot \vec{r}_z\right],
\]

\[
I = |U(P)|^2 = |U^*(P)|^2.
\]

The position of the intensity maxima around spherical scattering points has been simulated from this model. Figure 3 presents the simulated image together with experiment SEM image. From the theoretical calculation we know that the interference between the scattered light and laser radiation proceeds availably and interference fringes will occur with a spacing corresponding to the wavelength of the laser at different incident angels.

As the incident angel is 0° and 30° respectively, the perfect annular structures on SiGe surface are induced by the optical interference, which is respond to the Si, Ge atoms at the bright fringes migrating and agglomerating along the fringes. However, due to the Eq. (3) \( I \propto \frac{1}{\rho} \), for the angel of 45°, the interference intensity may decay fast along the propagation direction of the spherical wave, and the forward fringes are diffuse in simulation results as well. So the interference intensity at the bright fringe cannot induce atoms migrate sufficiently, and it forms the semi-annular structures ultimately. For the case of 60° incident angle, the forward fringes present at a more diffuse state as can be seen in simulated results. This implies that the interference intensity of the laser on SiGe surface is also diffuse, which results in the unobvious ripple structures at the forward position. At the backward position, the interference phenomenon becomes unobvious due to the larger density of bright fringes.
Under this condition, consequently, thermal effect of the laser beam begins to dominate the formation of the disorder island structures at the backward position.

![Figure 3](image1)

**Fig. 3.** Imagines of the comparison diagram of experiment and simulated results with single scattering point at different incident angels.

The beam scattered by every scattering point can be treated as spherical wave when there are several scattering points on the surface. We consider three scattering points for simulation, and then obvious interference phenomenon occurs around scattering points. The time-averaged interference intensity is given by:

\[
U(P) = U_x(P) + U_y(P) = A_\lambda \exp(j k \cdot \vec{r}_x) + \frac{A_1}{r_1} \exp(j k \cdot \vec{r}_1) + \frac{A_2}{r_2} \exp(j k \cdot \vec{r}_2) + \frac{A_3}{r_3} \exp(j k \cdot \vec{r}_3)
\]  

(4)

![Figure 4](image2)

**Fig. 4.** Imagines of the comparison diagram of experiment and simulated results at normal incident angle.

Figure 4 is the comparison diagram of experiment and simulated results at normal incident. The shapes of the annular structures are consistent with the optical interference fringes and these structures completely record down the optical interference information. This implies that the spherical waves around scattering points propagate radially on SiGe surface and interact with the incident beam. The interference phenomenon induces the redistribution
of the laser energy on the surface, which causes the migration and agglomeration of atoms along the interference fringes. The nature of the generated electromagnetic field structures and their relation to the simple “surface-scattered wave” model for periodic surface damage are discussed. The nature of the most likely initial perturbation is in height. Intuitively, the “surface-scattered wave” model is realistic in the limit where $l/\lambda$ is small ($l$ is the height of scattering points) [20]. Considering the surface damages induced by thermal stress from absorbing inclusions after laser irradiation and the loss of hot carriers due to diffusion outside the discharge volume [21,22], the minimum height of surface defects on the surface scattering center below the surface is about 10 nm.

From above analysis, the backward annular structures are replaced by disorder islands after the irradiation at 60° incident angle. We indicate that the thermal effect of the laser beam begins to dominate the formation of the island structures when the laser energy is larger than a threshold. Next, we investigate effects of different incident laser energies on the surface nanoscale structures. Figure 5 summarizes the observations of surface nanoscale structures, which are induced by different irradiation energy intensities at incident angle of 30°. We observe via those four images that only when the sample is irradiated at certain energy, perfect surface annular structures can be created. With the laser energy intensity increasing, a droplet-like morphology become the dominant feature, which will completely replace the surface annular structures for pulse energy beyond 230mJ/cm², regardless of the presence or absence of defects, like Figs. 5(c)-5(d). Owing to its randomness, this can no longer be interpreted by the theory of the optical interference between surface scattered light and incident laser. Actually, it is the thermal effect that induces the formation of disorder islands under this condition. It has been demonstrated that thermal effect accelerates the relaxation of strain, which finally forms disorder surface islands. And the disorder SiGe islands appear on the surface which caused by obvious lattice distortion between the SiGe islands and SiGe film. We estimate this condition on the surface exposure corresponds to the melting when surface tension is driving the formation of droplet-like morphology on the surface [23–26]. What we have obtained shows that the KrF excimer laser-patterned nanoscale structures on SiGe material are sensitive to pulse energy intensity, and diverse nanoscale structures appear coupling with different laser radialization energy ranges.

![Fig. 5. SEM images of annular structures generated on SiGe surface by KrF excimer laser with 30° incident angel at different energy density. (a): 90mJ/cm², (b): 150mJ/cm², (c): 230mJ/cm², (d): 230mJ/cm², respectively.](image)

4. Conclusion

In conclusion, we show that nanoscale structures on the SiGe film could generate if irradiated with multiple pulses. We prove that the surface annular structures are induced by interference between the scattered light and incident beam, and the observed structures can record down the information of optical interference. Then, we demonstrate that the shapes of annular structures are related to the energy distribution via simulation according to the theory of the optical interference. Finally, while the laser pulse energy exceeds a certain threshold, thermal effect will take place and result in the formation of droplet-like morphology on SiGe surface. Our results give a detail relationship between laser irradiation and the formation of nanoscale structures, which provides deeper insight into the physical processes involved in the generation of such complex laser-induced nanostructures.
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