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Laser induced formation of periodic nanostructures in silicon covered by SiO_2

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ABSTRACT Three-dimensional (3D) and two-dimensional (2D) periodic silicon nanostructures formed by polarized focused Nd:YAG laser irradiation (532 nm) with spot size less than 3 μm on Si covered by SiO_2 are presented in this paper. We observed that at a low laser intensity I range, from $I = 0.9$ to 1.08 W, 2D periodic coexisting of liquid and solid exists, while for $1.08 < I < 1.44$ W, 3D periodic ripples were formed. However, when the light intensity is out of those ranges, either no melting was created ($I < 0.9$ W) or the periodicity was destroyed ($I > 1.44$ W). The periodicity of these periodic structures is 359 nm related to the wavelength of frequency doubled Nd:YAG laser and the index of refraction of SiO_2. We propose a model based on the fact that as the oxygen is diffusing locally from SiO_2 into the melted Si, thus forming SiO_β with a lower melting point, successive pulses melt preferentially these regions giving rise to a positive feedback. This dynamic nanoscale modeling, based on variations of melting points of Si and dielectric and reflection coefficient, confirms the experimental results.

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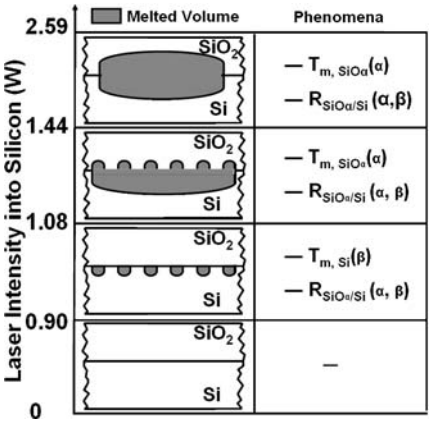

FIGURE 1 Schematics of formation of periodic structures depending on laser intensity and positive feedback factors. See the text for the explanation on the phenomena

1 Introduction

Spontaneous ripples [1–6], formed after intense irradiation of a single or multiple laser beam(s) operating at wide optical wavelengths, with pulse durations ranging from continuous wave (cw) to picosecond pulses [5–13], were frequently observed on the blank surface of a variety of materials [2, 3, 8, 11, 13–21], such as dielectrics, semiconductors and metals, and were considered as a mixture of solid and liquid at a temperature close [1] to the melting threshold. Emmony et al. [3] for the first time proposed that a scattering center on the surface might be responsible for the observed periodic topography. It has been suggested that theses ripples [3] arise from standing waves produced by one instability and developed as a result of interference of incident laser light with scattered electromagnetic waves from a surface disturbance [2, 10, 11]. The ripple periods are mostly found to follow Rayleigh's diffraction criterion [11, 13].

In this paper, we report the formation of periodic nanostructures in Si covered by SiO_2. In our case the polarized laser beam is normal to the sample surface therefore the periodicity of the nanostructures, including coexisting of liquid and solid as well as ripples, is $\Lambda = \lambda/n$ [13], where Λ is the wavelength of the standing wave and thus the periodicity of our nanostructure, λ is the laser wavelength, and n (~ 1.5) is the refractive index of SiO_2. We observed not only ripples but also flat coexisting of solid and liquid, formed by a focused (in diameter of 3 μm) frequency doubled Nd:YAG laser ($\lambda = 532$ nm) under different light intensities schematically shown in Fig. 1. The proposed formation mechanisms of the two phenomena with periodicity of ~ 359 nm, which is different from the previous studies [25], are based on a locally and spatially periodic oxygen diffusion induced by the laser irradiation as it is clearly revealed by chemically selective etching. A model, supported by a three dimensional (3-D) numerical simulation, is proposed to explain the formation mechanisms of the periodic nanostructures.

2 Experimental details

Samples were obtained by conventional microelectronics fabrication flow and consisted of a gateless field effect transistor where the silicon is covered by many dielectric layers, including SiO_2, SiO_xN_y, and Si_3N_4. Two heavily doped p-type regions (boron concentration at $\sim 5 \times 10^{19}$ atoms/cm^3) have a doped depth of 170 nm and are separated by a lightly As doped gap (concentration at $\sim 10^{15}$ atoms/cm^3)

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with a distance of 600 nm. This structure is more commonly used in the laser induced dopant diffusion to form a highly accurate resistance for analogue microelectronics [22]. This structure is also helpful to reveal the nanostructures based on oxygen diffusion. The TEM (transmission electron microscopy) and SEM (scanning electron microscopy) samples were prepared by a HITACHI FB-2000A focused ion beam (FIB) instrument using Ga ion beam milling. The main advantage in this sample preparation is that the interesting area, involving the interface between the oxide and the Si substrate (for TEM observation) and, the gap location (for SEM observation), can be precisely located. After FIB preparation, the samples were etched using HF (49%) and HNA [HF(49%) : HNO_3(70%) : CH_3COOH(80%) = 1 : 3 : 8] for TEM and SEM observations. For AFM imaging, the dielectrics layers above Si in the samples were etched by HF (49%). The etching rate of Si in solution of HNA is extremely higher than that of dielectric materials.

3 Results and discussion

We observed two types of topographic phenomena, as shown in the AFM images in Fig. 2 taken after etching the dielectric multilayers using HF solution. The laser intensities, irradiated on two samples, were 3 and 4 watts, respectively, and the pulse number (100 pulses), pulse width (80 ns), and irradiation duration (100 µs) and diameter of the focused laser beam (3 µm) are the same for both cases. Using light reflection measurement, we estimated that for this sample structure, 36% of the laser energy was absorbed by the top thin Si layer. Therefore, the flat and 3D topographies shown in Fig. 2a and b were created under irradiation of 1.08 W and 1.44 W, respectively. We suggest that these two cases represent two different mechanisms.

It is important to note first that it can be extracted from a Si-O phase diagram [24], the melting point of silicon with a composition of SiO_β decreases from 1417 °C for pure Si to a eutectic temperature of 1300 °C with dependence of $T_{m,\mathrm{Si}}(\beta) = 914 + 503/(1+\beta)$ for $0 < \beta < 0.3$ and the melting point of oxide with a composition of SiO_α decreases from 1725 °C to 1450 °C with dependence of $T_{m,\mathrm{SiO}_\alpha}(\alpha) = 3022 - 3929/(1+\alpha)$ for $1.5 < \alpha < 2$ when O concentration decreases. Note that the melting temperature dependence on boron was neglected because the B concentration was relatively low [24]. While all previous studies [6, 8, 26, 27] were carried on topographic formation by laser irradiated on blank material surfaces, we propose that the gateless MOSFET structure having a SiO_2 layer and B implanted regions has a special contribution by furnishing oxygen diffusion, yielding to a local lower melting point and reflection coefficient that enhances the periodic nanostructure formation. Since no ripples were observed by AFM in Fig. 2a for $I < 1.08$ W, we performed plan-view TEM sample on 170 nm thick defective Si surface to investigate the microstructure generated under those laser conditions. The TEM bright-field image as shown in Fig. 3a indicates the phenomenon of the coexisting of liquid and solid during laser irradiation process. The white gap along the y axis corresponds to the lightly n-doped region without defective contrast. The six white stripes along the x axis were formed because the implantation-induced defects were removed after laser annealing. However, the alternate areas beside the regrown stripes remained in their solid phase during irradiation. This laser induced coexisting of liquid and solid did not cause ripple topography as indicated in

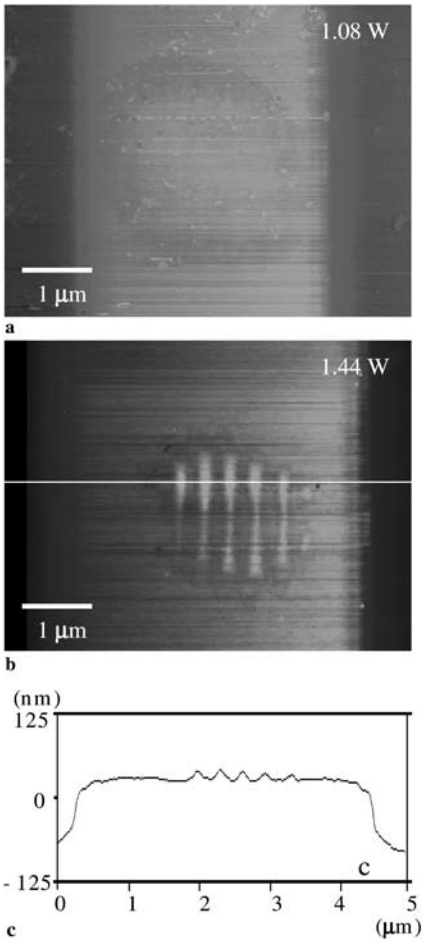

FIGURE 2 (**a**) and (**b**) AFM images taken after etching dielectrics layers using HF solution show topographies of laser irradiated samples. Those topographies were formed at laser intensities of 1.08 W (**a**) and 1.44 W (**b**); figure (**c**): height delineation along the line as shown in (**b**)

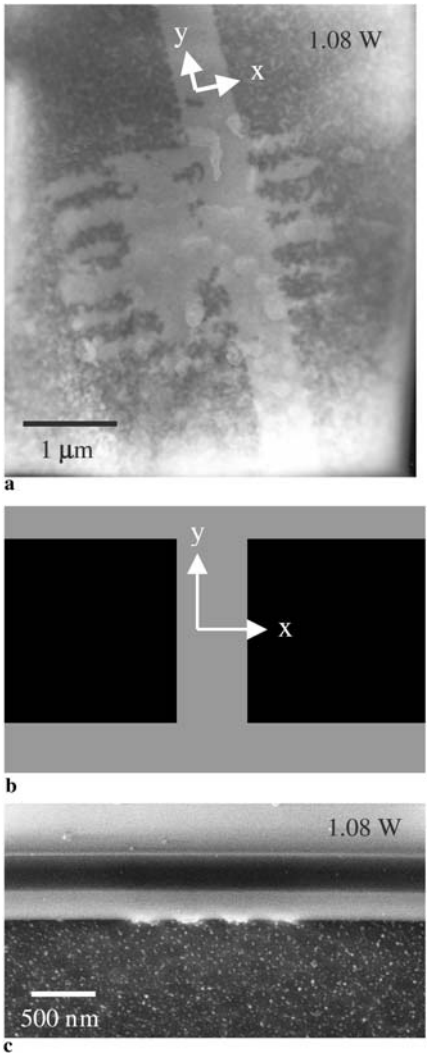

FIGURE 3 (**a**) Plan-view TEM image taken from a laser irradiated sample, (**b**) top-view schematics of Si substrate used in (**a**) process, where the areas with dark contrast are heavily doped regions, and (**c**) SEM image taken from a laser irradiated sample and FIB-prepared along y axis. The two samples were generated with laser intensity of 1.08 W

our AFM measurement above (Fig. 2a), which is different from those suggested by some authors for laser irradiation on blank silicon materials [1–5].

Figure 3c shows a cross-sectional SEM images of a FIB-prepared sample, along the y axis shown in Fig. 3b, taken after 2 seconds of HNA etching. The sample was produced with the same laser parameters as that shown in Fig. 3a. In Fig. 3c, because the As and diffused B concentrations at the Si surface of the gap are much lower than O concentration, the difference of etching rate mainly depends on the O profile. The four periodic white meniscus-like shapes indicated the regrowth regions where O atoms highly diffused from the SiO_2 into Si. The melting stripes close to the edge of the laser beam, containing less O atoms, are not revealed by SEM imaging.

The formation of aligned coexisting of liquid and solid depends mainly on the variations of the Si melting point ($T_{m,\mathrm{Si}}(\beta)$) and reflection coefficient ($R_{\mathrm{SiO}_\alpha-\mathrm{Si}}$) of the liquid, related to the chemical components of dielectric and the liquid. Under laser irradiation with relatively low intensity (e.g., 1.08 W) and based on standing wave theory [2, 10, 11], the Si material under the dielectric layer is periodically melted and O atoms diffuse into the molten stripes, caused by a light intensity variation. After the first few laser pulses, the melting point of the regrown strips is lowered, favoring the O atoms to diffuse from the hot dielectric into the melt faster than those into hot solid Si because the diffusion length of impurities in liquid Si is four orders of magnitude higher than that in solid Si [29]. The O impurities lower both the melting point of solid Si and the reflectivity of Si liquid. Consequently, this constitutional supercooling [23] act as positive feedback factors, leading to a periodic coexisting of liquid and solid.

In order to verify our suggestion on the formation mechanisms of the periodic coexisting of solid and liquid, a 3D numerical simulation of the temperature field and optical reflection [30] was performed in combination with diffusion equations of oxygen atoms. We found that it was impossible to obtain any periodic nanostructures if the Si melting temperature is independent of the O concentration. However, as shown in Fig. 4, periodic nanostructures, as observed experimentally, are obtained when the melting temperature depends on the O concentration. The contrast in the melting strips indicates the O concentration level.

As shown in Fig. 1, at higher laser intensity, a different periodic pattern is observed. From the TEM observation (not shown here), it is confirmed that for the case of $I = 1.44$ W, Si material in the entire laser irradiated area was melted. After the radiation of the first consecutive laser pulses, the light reflection from the liquid of the periodically highly O diffused areas was weakened as a result of O gain in the liquid Si and O loss in the dielectric close to the interface. Therefore, the temperature in the liquid is periodically higher than the melting point of pure Si whereas the temperature in the stripes with lower O concentration is maintained at the melting point by considering the energy input from laser beam and output to the Si substrate. The melting temperature in these dielectric areas ($T_{m,\mathrm{SiO}_\alpha}(\alpha)$), where O atoms were extremely lost, is lowered so that these thin SiO_α stripes were periodically melted. The gradients of temperature and chemical components between the two type areas with higher and lower O concentrations lead to a difference of surface tension, pushing individually each stripe, where O concentration is higher, forming semilunar shapes (so-called periodic convection), which is similar to the case suggested by Anthony et al. [28]. By further increasing the laser intensity ($I > 1.44$ W), the periodic formation is destroyed, as indicated in Fig. 1, since O atoms almost uniformly diffuse into the entire laser-melted area. In these conditions, a large liquid convection occurs in the entire molten volume involving both liquid Si and liquid dielectric.

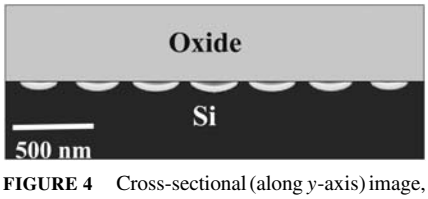

FIGURE 4 Cross-sectional (along y-axis) image, showing the solid/liquid coexisting of the laser irradiated area, was obtained by numerical simulation

Based on our numerical simulations, it is shown that the melting time, caused by each laser pulse, is ~ 200 ns and, since the time between two consecutive pulses is 1 μs the interval between two adjacent melting periods is about 800 ns. Even though the interval is pretty long to let the molten Si resolidify, both periodic liquid/solid coexistings and ripples, with spacing of 359 nm, can still be created by considering the decrease of Si melting point due to O diffusion.

4 Conclusions

We suggest that the major positive feedback factors of the formations of solid/liquid coexisting and ripple are oxygen diffusion and reflectivity variation. In our experimental study the periodic melting is more prominent at a low intensity range while ripples are obvious at a relatively high intensity range. According to the mechanisms above, we suggest both periodic coexisting and ripples can be formed not only by many laser pulses with certain pulse interval but also by a single laser pulse with adequately high energy intensity. The final steady-state structures depend on the competition between positive feedback factors and the removal or redistribution of energy due to thermal conduction. Generalizing this fabrication of nanostructures, coexisting could occur for any material A covered by an alloy AB if it presents an eutectic temperature for AB_x, lower than the melting temperature of A point. The periodicity will be destroyed once melting time is too long due to too high power or too many laser pulses.

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REFERENCES

1 M. Combescot, J. Bok, Phys. Rev. B **29**, 6393 (1984)
2 M. Birnbaum, J. Appl. Phys. **36**, 3688 (1965)
3 D.C. Emmony, R.P. Howson, L.J. Willis, Appl. Phys. Lett. **23**, 598 (1973)

4 C.T. Walters, Appl. Phys. Lett. **25**, 696 (1974)
5 N.R. Isenor, Appl. Phys. Lett. **31**, 148 (1977)
6 S. Theppakuttai, S. Chen, J. Appl. Phys. **95**, 5049 (2004)
7 F. Keilmann, Y.H. Bai, Appl. Phys. A **29**, 9 (1982)
8 G.N. Maracas, G.L. Harris, C.A. Lee, R.A. McFarlane, Appl. Phys. Lett. **33**, 453 (1978)
9 H. Varel, M. Wahmer, A. Rosenfeld, D. Ashkenasi, E.E.B. Campbell, Appl. Surf. Sci. **128**, 127 (1998)
10 J.F. Young, J.E. Sipe, J.S. Preston, H.M. van Driel, Appl. Phys. Lett. **41**, 261 (1982)
11 P.M. Fauchet, A.E. Siegman, Appl. Phys. Lett. **40**, 824 (1982)
12 J. Ihlemann, B. Wolff, P. Simon, Appl. Phys. A **54**, 363 (1992)
13 Z. Guosheng, P.M. Fauchet, A.E. Siegman, Phys. Rev. B **26**, 5366 (1982)
14 J.E. Sipe, J.F. Young, J.S. Preston, H.M. van Driel, Phys. Rev. B **27**, 1141 (1983)
15 H.J. Leamy, G.A. Rozgonyi, T.T. Sheng, G.K. Celler, Appl. Phys. Lett. **32**, 535 (1978)
16 D. Haneman, R.J. Nemanich, Solid State Commun. **43**, 203 (1982)
17 P.A. Temple, M.J. Soileau, IEEE J. Quant. Elec. **QE-17**, 2067 (1981)
18 M. Oron, G. Sorensen, Appl. Phys. Lett. **35**, 782 (1979)
19 P.M. Fauchet, A.E. Siegman, Appl. Phys. Lett. **40**, 824 (1981)
20 T.E. Zavecz, M.A. Saifi, Appl. Phys. Lett. **26**, 165 (1975)
21 J.C. Koo, R.E. Slusher, Appl. Phys. Lett. **28**, 614 (1976)
22 M. Meunier, Y. Gagnon, Y. Savaria, A. Lacourse, M. Cadotte, Appl. Surf. Sci. **186**, 52 (2002)
23 M.A. Bosch, R.A. Lemons, Phys. Rev. Lett. **47**, 1151 (1981)
24 H.F. Wolf, *Silicon Semiconductor Data* (Pergamon, Oxford, 1969)
25 R.J. Nemanich, D.K. Biegelsen, W.G. Hawkins, Phys. Rev. B **27**, 7817 (1983)
26 J.F. Young, J.E. Sipe, H.M. van Driel, Opt. Lett. **8**, 431 (1983)
27 J.A. van Vechten, Solid State Commun. **39**, 1285 (1985)
28 T.R. Anthony, H.E. Cline, J. Appl. Phys. **48**, 3888 (1977)
29 H. Kodera, Jpn. J. Appl. Phys. **2**, 212 (1963)
30 J.-Y. Degorce, J.-N. Gillet, F. Magny, M. Meunier, J. Appl. Phys. **97**, 033 520-1 (2005)