Ge films grown on Si substrates by molecular-beam epitaxy below 450 °C

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Ge thin films are grown on Si(001) substrates by molecular-beam epitaxy at 370 °C. The low-temperature epitaxial growth is compatible with the back-end thermal budget of current generation complementary metal-oxide-semiconductor technology, which is restricted to less than 450 °C. Reflection high-energy electron diffraction shows that single-crystal Ge thin films with smooth surfaces could be achieved below 450 °C. Double-axis x-ray $\theta/2\theta$ scans also show that the epitaxial Ge films are almost fully strain-relaxed. As expected, cross-sectional transmission electron microscopy shows a network of dislocations at the interface. Hydrogen and oxide desorption techniques are proved to be necessary for improving the quality of the Ge films, which is reflected in improved minority carrier diffusion lengths and exceptionally low leakage currents. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1738530]

Recent advances in epitaxial technologies, coupled with an increasing demand for optoelectronic integration, have made Si-based optoelectronic devices very important. Epitaxial Ge films on Si substrates can be used as photodetectors for the important 1.3 or 1.55 μm optical communications window.[1–4] It is especially beneficial if Ge epitaxy can be carried out in a manner that is compatible with the back-end processing of Si complementary metal-oxide-semiconductor (CMOS), which has an upper temperature limit of 450 °C. It should be noted that various deposition techniques, such as using hydrogen[5] or Sb[6] as surfactants, cyclic thermal annealing,[4,7] selective area growth,[8] or Si capping layers,[9] etc., have been employed for epitaxial growth of Ge on Si with very good results. The problem is that the growth temperature used in these techniques exceeds the ceiling temperature of 450 °C. Practically the only publications[3,10] with $T<450$ °C use thermal evaporation, and the resulting Ge/Si photodetectors show moderate performance. Compared to thermal evaporation, molecular-beam epitaxy (MBE) has the advantage of much lower background pressure and growth rate, leading to increased latitude in optimizing the growth conditions for enhanced device performance. In addition, Eaglesham *et al.*[11] have already proved the possibility to obtain crystalline Ge films on Si at low temperature by MBE.

In the context of thin films grown for photodetector applications, there are two major points of concern: the optical absorption coefficient and the lifetime or diffusion length of minority carriers in the epitaxial layer. The absorption coefficient α of the epitaxial Ge might deviate from its desired value (that of bulk Ge), if the Ge film is partially strained. The minority carrier lifetime τ or diffusion length L_D is determined by the crystalline quality of the Ge which, in turn, depends on the overall density of various defects including stacking faults, dislocations, and point defects.

In this letter, we report on the growth of epitaxial Ge films on Si(001) at 370 °C using several predeposition desorption techniques. The quality of the Ge films is gauged by estimating the minority carrier diffusion length through responsivity measurements on p-Ge/n-Si photodetectors. Figure 1 shows the schematics of the sample structure. The incident light has a wavelength of 1.31 μm and is therefore absorbed only by the Ge. Since the doping concentration in the Ge layer is much higher than in the substrate, the depletion region is mainly in the Si. As a result, the responsivity is derived mainly from diffusion inside the Ge and the photocarriers generated within one L_D of the Ge/Si interface are the only ones that will be efficiently collected. Therefore, in our experiments, L_D is deduced from the responsivity by equating the measured internal quantum efficiency to the fraction of light absorbed within one diffusion length of the interface. All our results are quoted in terms of the diffusion length and not the responsivity because we feel that the former is a much better indicator of germanium quality. Responsivity is not as fundamental because along with being dependent on the quality of the material it is also a strong function of the device design and wavelength. In addition to diffusion length measurements, structural characterization of the Ge films is done using transmission electron microscopy (TEM), *in situ* reflection high-energy electron diffraction (RHEED) and x-ray $\theta/2\theta$ scans.

We grow relaxed Ge films on n-type Si substrates using a Riber EVA-32 MBE. The base pressure of the MBE growth chamber is 5×10^{-10} Torr. The substrates are n-type (001)Si. All the samples are cleaned with the modified Piranha method.[12] A small difference between the various samples is introduced in the last step of the cleaning process. The final wet-chemical cleaning step for samples M5, M7, M9, and

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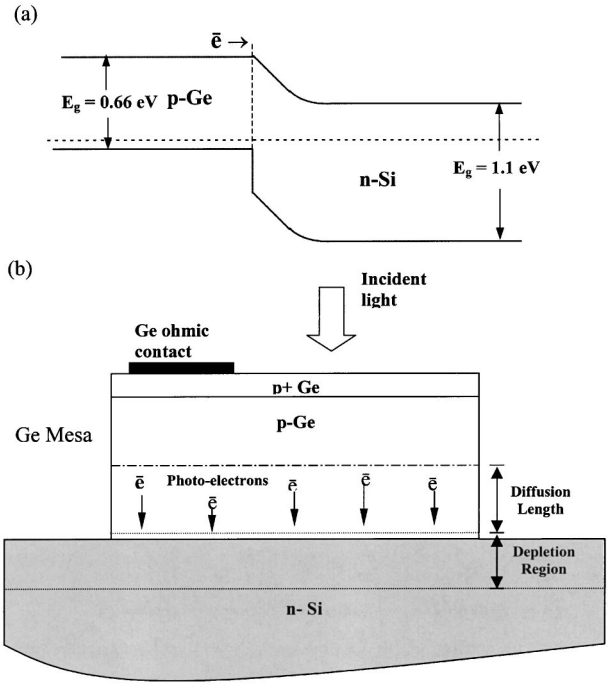

FIG. 1. (a) Proposed band alignment that is consistent with our experiments. The depletion region is completely in the silicon. (b) Schematic diagram of the growth structure. Photoelectrons diffuse towards the depletion region.

M12 is an HF dip leading to a hydrogen-terminated surface. Sample M3, on the other hand, is dipped in Piranha in the final step, and hence its surface is oxygen terminated. The Ge growth conditions for all the samples are summarized in Table I.

In each sample, the first 190 nm of the germanium is doped *p*-type with the final 10 nm being doped p^+ in order to reduce the metal–Ge contact resistance in the photodetectors. The Ge growth is monitored throughout by *in situ* RHEED. The RHEED pattern gradually changes from three-dimensional to (1×1) and then to (2×1) during the Ge deposition process. All the samples show a reasonably sharp (2×1) pattern at the end of the Ge growth. Figure 2 shows a typical (2×1) RHEED pattern taken after the completion of the Ge deposition. Double-axis x-ray measurements were taken on a Bede D3 diffractometer using $\mathrm{Cu\,K}_{\alpha1}$. Figure 3 shows the results for samples M9, M7, M12, and M3. For Ge films grown on Si, there are two kinds of strain: the compressive strain, which is caused by the lattice mismatch, and the tensile strain, which is introduced by thermal mismatch.[13] In our case, the strain accumulated by thermal mismatch is

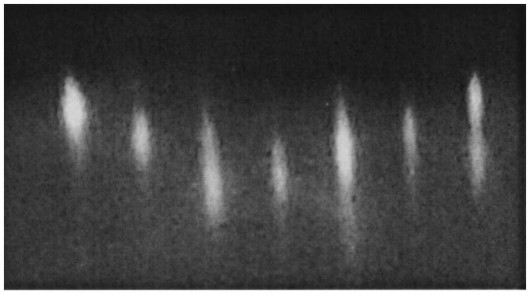

FIG. 2. Clear (2×1) RHEED pattern after the completion of the Ge growth (at 370 °C). The pattern indicates the formation of a single-crystal film.

very small because of the low growth temperature. An estimate of the Ge lattice constant from each curve indicates that the Ge film in all the samples is almost completely relaxed. These results ensure the validity of using the band structure of bulk Ge in analyzing the photoresponse.

Figure 4 shows the cross-sectional TEM pictures for samples M3, M7, M9, and M12. Due to the 4% lattice mismatch between Si and Ge, there is a network of dislocations at the Ge/Si interface. Although it is impossible to count the number of dislocations at the interface precisely, we can get a rough estimate of the density of dislocations at the middle of the Ge layer. From Figs. 5(a)–5(d), we see that this density is $\sim 4\times10^{10}\,\mathrm{cm}^{-2}$ in all the samples. The combined structural characterization using RHEED, x-ray diffraction (XRD), and TEM show no observable difference in terms of the density of extended defects among samples grown in different ways.

Figure 5 gives the diffusion length values obtained from photodetectors made out of each sample. It is seen that the oxide and hydrogen desorption steps cause a reasonable increase in the value of L_D. Even though the 800 °C anneal is clearly most effective in enhancing L_D, the growth conditions used for samples M7 and M12 are deemed optimum because they are compatible with back-end CMOS processing. The value of L_D for these two samples ($\sim$25 nm) compares favorably with typical values reported for low temperature growth of Ge on silicon. The changes in L_D are not reflected in the structural characterization using RHEED, XRD, and TEM, because an increase in L_D indicates an improvement in the Ge quality very close to the Ge/Si interface (within $\sim$20–30 nm). In the vicinity of the interface, the density of dislocations is too high to be effectively quantified by the structural analysis techniques used in our measurements. The improvement in L_D most likely corresponds to a

TABLE I. Pregrowth processing conditions for each sample. After the desorption step, Ge deposition (200 nm at 0.2 Å/s) in all the samples was done using MBE at 370 °C. The prefix M denotes growth by MBE. The samples are numbered in the order in which they were grown.

Sample	Sample cleaning	Pregrowth condition
M5	HF finish	No desorption treatment
M9	HF finish	200 °C hydrocarbon desorption for 50 min
M7	HF finish	450 °C hydrogen desorption for 15 min
M12	HF finish	Both 200 °C hydrocarbon desorption for 50 min and 450 °C hydrogen desorption for 15 min
M3	Piranha finish	800 °C oxide desorption

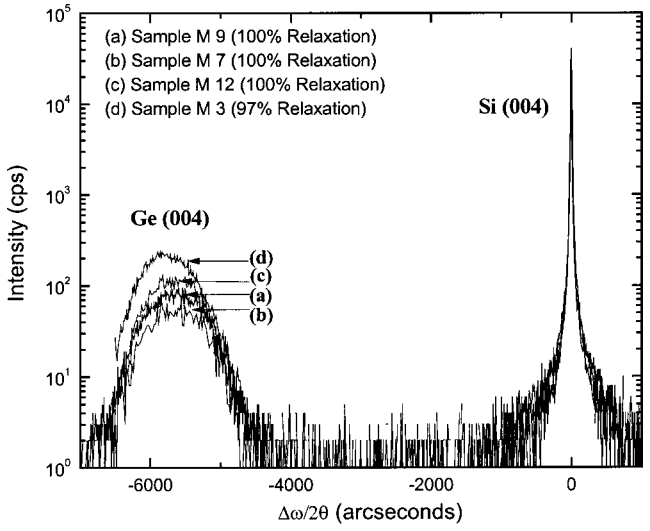

FIG. 3. (004) double-axis x-ray $\theta/2\theta$ curves of (a) sample M9, (b) sample M7, (c) sample M12, and (d) sample M3. Table I gives an exact description of the pregrowth desorption process for each sample. The peak position of the Si substrate is taken to be zero.

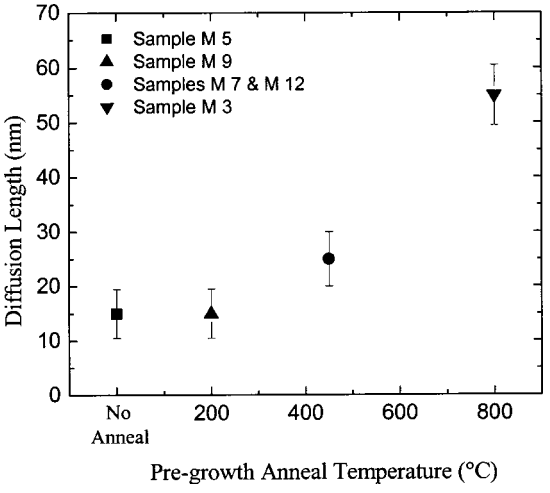

FIG. 5. Diffusion length versus "pregrowth" anneal temperature. All samples were grown by MBE at 370 °C with the same structure and growth rate (0.2 Å/s).

decrease in the number of interfacial point defects such as C precipitates and other kinds of inclusions typically associated with imperfectly cleaned surfaces.

The measured dark current values in all the samples were found to be roughly equal (~0.2 to 0.3 mA/cm^2 at −1 V). These values are a factor of 4 lower than those reported by Masini *et al.*[3] and are comparable to the dark currents expected from bulk Ge.

In conclusion, we have investigated the growth of Ge films on Si at temperatures (370 °C) that are compatible with the back-end thermal budget of current generation CMOS technology. The double-axis x-ray $\theta/2\theta$ curves show that the epitaxial Ge film is almost fully relaxed, which in turn ensures that the optical absorption properties of the Ge films are similar to those exhibited by bulk Ge RHEED patterns and TEM pictures were used to gauge the crystalline quality of the Ge films, and they were found to be single crystal. Measurements on simple $p-n$ junction photodetectors show that reasonable performance can be expected from the Ge films. Hydrogen and oxide desorption techniques are useful in enhancing the quality of the epitaxial Ge, with the latter producing quite significant improvements.

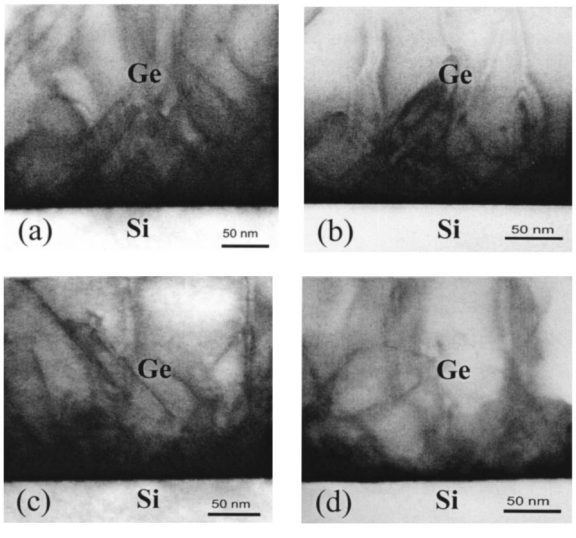

FIG. 4. Bright field cross-sectional TEM images of (a) sample M9, (b) sample M7, (c) sample M12, and (d) sample M3. Table I gives an exact description of the pregrowth desorption process for each sample.

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[1] L. Colace, G. Masini, F. Galluzzi, G. Assanto, G. Capellini, L. Di Gaspare, E. Palange, and F. Evangelisti, Appl. Phys. Lett. **72**, 3175 (1998).
[2] L. Colace, G. Masini, F. Galluzzi, G. Assanto, G. Capellini, L. Di Gaspare, E. Palange, and F. Evangelisti, J. Vac. Sci. Technol. B **17**, 465 (1999).
[3] G. Masini, L. Colace, F. Galluzzi, and G. Assanto, Mater. Sci. Eng., B **69**, 257 (2000).
[4] S. Famà, L. Colace, G. Masini, G. Assanto, and H.-C. Luan, Appl. Phys. Lett. **81**, 586 (2002).
[5] A. Sakai and T. Tatsumi, Appl. Phys. Lett. **64**, 52 (1994).
[6] J. L. Liu, S. Tong, Y. H. Luo, J. Wan, and K. L. Wang, Appl. Phys. Lett. **79**, 3431 (2001).
[7] H.-C. Luan, K. Wada, L. C. Kimerling, G. Masini, L. Colace, and G. Assanto, Opt. Mater. (Amsterdam, Neth.) **17**, 71 (2001).
[8] H.-C. Luan, D. R. Lim, K. K. Lee, K. M. Chen, J. G. Sandland, K. Wada, and L. C. Kimerling, Appl. Phys. Lett. **75**, 2909 (1999).
[9] A. Sakai, T. Tatsumi, and K. Aoyama, Appl. Phys. Lett. **71**, 3510 (1997).
[10] L. Colace, G. Masini, and G. Assanto, Appl. Phys. Lett. **82**, 2524 (2003).
[11] D. J. Eaglesham and M. Cerullo, Appl. Phys. Lett. **58**, 2276 (1991).
[12] The exact cleaning procedure is as follows: First the substrate is dipped in Piranha ($H_2O_2:H_2SO_4=3:5$) for 1 min and then in aqueous HF solution ($HF:H_2O=1:10$) for 1 min. This procedure is then repeated three times.
[13] Y. Ishikawa, K. Wada, D. D. Cannon, J. Liu, H.-C. Luan, and L. C. Kimerling, Appl. Phys. Lett. **82**, 2044 (2003).