All laser-assisted heteroepitaxial growth of $Si_{0.8}Ge_{0.2}$ on Si(100): Pulsed laser deposition and laser induced melting solidification

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The growth of heteroepitaxial $Si_{0.8}Ge_{0.2}$ films on Si(100) by a novel all laser-assisted technique using only ArF excimer laser radiation is demonstrated. Amorphous 30 nm thick films are grown by pulsed laser deposition from alternating pure Si and Ge targets on clean Si substrates. Melting and rapid solidification is then induced by pulsed irradiation (0.54 J/cm^2), promoting epitaxial growth.
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Over the last years there has been a rapid progress in the fabrication of high-speed heterojunction bipolar transistors using the narrow band-gap $Si_{1-x}Ge_x$ layers grown on Si(100). Presently the research has been mainly focused on the use of molecular beam epitaxy and chemical vapor deposition. While these techniques have demonstrated growth of device quality material, the microelectronic technology has an increasing demand for higher integration. The reduction of the substrate temperature, or of the processing times, are desirable in order to minimize impurity diffusion and to avoid junction destruction. In this context, pulsed laser assisted epitaxy of $Si_{1-x}Ge_x$ alloys was proposed at the end of the 1980's.[1] Despite the fact that the surface is heated above the melting temperature, laser-induced heating occurs over a relatively short period of time (<100 ns) and affects only the near-surface region. This technique has been successfully applied to produce strained layers of heteroepitaxial $Si_{1-x}Ge_x$ starting from e-beam deposited amorphous Ge or $Si_{1-x}Ge_x$ alloys.[1–5]

In this letter, we aim to show the use of laser assisted epitaxy for films also deposited by a laser assisted technique: pulsed laser deposition (PLD). PLD has undergone a rapid progress during the last decade because, being conceptually a simple technique with very limited experimental requirements, it has been demonstrated to be very successful for the deposition of complex compounds.[6] An attempt to directly grow heteroepitaxial $Si_{1-x}Ge_x$ layers from a $Si_{0.8}Ge_{0.2}$ target on heated silicon substrates has already been reported.[7,8] The temperature of the substrate was a critical parameter, and the films presented a Ge enrichment ($x \approx 0.45$) compared to the initial composition of the target. In the present work, PLD from pure and independent Si and Ge targets is used to deposit alternate layers of Si and Ge on a room-temperature Si substrate. The deposition from two independent targets allows an easy control of the final film composition. The as-grown films are amorphous and are laser irradiated to induce melt, diffusion, and heteroepitaxial crystallization of a high Ge concentration ($x = 0.20 \pm 0.02$) alloy.

PLD of $Si_{1-x}Ge_x$ was performed in a vacuum chamber with a base pressure of 4×10^{-7} Torr. The beam from an ArF excimer laser (Questek 2440, 193 nm, 12 ns FWHM) was focused onto the targets surface, leading to energy densities of about 3 J/cm^2 per pulse. The Ge (99.999%) and Si (<99.999%) targets were both rotated during deposition in order to avoid crater formation and droplet/particles emission.[9] The *p*-type Si(100) substrates were RCA cleaned, and immediately prior to loading into the chamber were dipped in a HF:Si water solution, in order to eliminate the surface oxide. The substrates were held at room temperature during deposition. A HeNe (632.8 nm) laser was used to perform *in situ* reflectance interferometry (RI) measurements, which allowed us to monitor sample thickness and deposition rates. The $Si_{1-x}Ge_x$ films were grown by alternate deposition of Si and Ge, and designed to reach an average composition of 20% Ge and a total thickness of 30 nm in 30 deposition periods, which is equivalent to alternating 0.8 nm Si and 0.2 nm Ge. The average deposition rates were 0.2 and 0.4 nm/s for Si and Ge, respectively, for a laser frequency of 5 Hz. Composition and total thicknesses of the as-deposited $Si_{1-x}Ge_x$ films were determined by Rutherford backscattering spectrometry (RBS) using a 1.6 MeV He^+ beam, with a backscattering angle of 140°. The RBS measurements show a total thickness of 30 ± 2 nm at the deposit center, and a Ge concentration corresponding to $x = 0.20 \pm 0.02$, both values in very good agreement with the RI measurements during film deposition. Individual layers of subnanometric dimensions could not be resolved in the described experimental conditions. For all the samples there is at least an area of 2×3 mm^2 at the deposit center in which the sample thickness varies less than 5% and the composition is uniform.[9] It must be noted that large area deposition with good homogeneity can be achieved easily either scanning the laser or rotating the substrate.[10]

The films were introduced in a vacuum chamber (4×10^{-5} Torr) to avoid surface oxide formation upon laser irradiation,[11,12] and irradiated with an energy density of 0.54 ± 0.05 J/cm^2 at the sample site. A HeNe beam laser at 25° off the normal incidence was used to monitor in real time the

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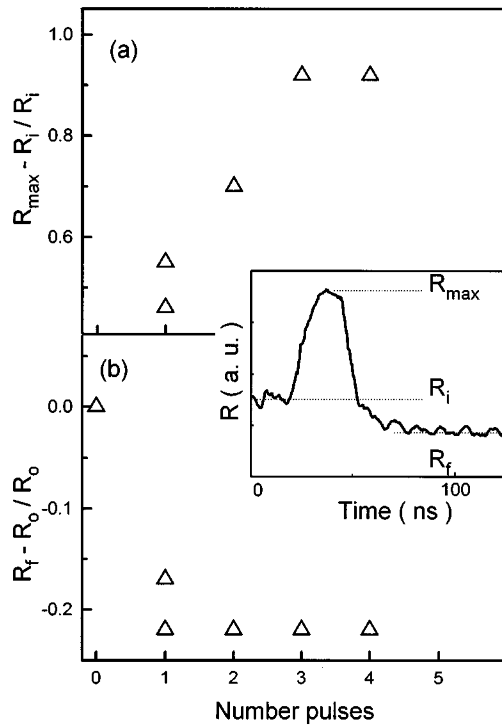

FIG. 1. Maximum transient reflectivity R_{max} normalized to the initial reflectivity level before each pulse R_i (a), and final reflectivity R_f normalized to the film reflectivity level before irradiation R_0 (b), determined from the real time reflectivity measurements, and plotted as a function of the accumulated number of pulses. The inset shows a typical reflectivity transient.

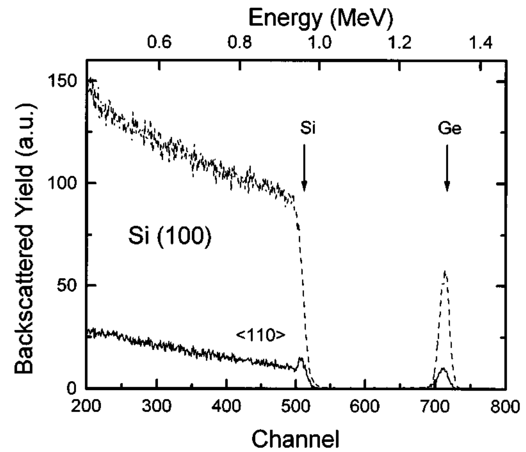

FIG. 2. RBS random (dashed line) and channeling (solid line) spectra for $Si_{0.8}Ge_{0.2}$ films grown on Si(100) by PLD and irradiated with four laser pulses. The channeling was performed in the ⟨110⟩ direction. The arrows indicate the surface channels for Si and Ge.

induced reflectivity changes,[13] while accumulating up to four pulses. Upon irradiation, characteristic reflectivity changes similar in shape to those previously reported for semiconductors (Si,[13,14] Ge,[14,15] and GaAs[16]) are observed [see inset in Fig. 1(a)]. The arrival of the laser pulse induces a reflectivity increase from the value at room temperature upon heating and melting of the surface. The maximum reflectivity is followed by a decrease due to the cooling and solidification processes. After solidification, the changes induced in the structure and/or composition upon irradiation lead to changes in the film reflectivity.

Figure 1 shows key features of the reflectivity transients as a function of the number of accumulated pulses. The maximum of the reflectivity transient (R_{max}) has been normalized to the initial reflectivity level before each pulse (R_i) and it is plotted in Fig. 1(a). The normalized R_{max} increases with the accumulated number of pulses and reaches a saturation value after two of them. The phase changes—the amorphous (a), liquid (l), and crystalline (c) phases of $Si_{0.8}Ge_{0.2}$—can be followed from these reflectivity transients. The reflectivity of c-$Si_{0.8}Ge_{0.2}$ at 632.8 nm is 0.36,[17] which is very close to that of c-Si, 0.35.[18] Although the reflectivity values for the amorphous and liquid phases are not known, it can be assumed that they will also be similar to those of a-Si (0.43)[19] and l-Si (0.70)[20] respectively. Upon $c \rightarrow 1$ transformation a relative reflectivity increase of 96% is expected, whereas an increase of only 63% is expected for the $a \rightarrow 1$ transformation. The measured normalized transient maximum reflectivity values [Fig. 1(a)] are consistent with a phase change $c \rightarrow 1$ upon irradiation with more than two pulses, whereas the value obtained for the first pulses is lower and is in good agreement with an $a \rightarrow 1$ phase change.[13,20] The final reflectivity value (R_f) normalized to the initial reflectivity level before irradiation (R_0) is plotted in Fig. 1(b). The normalized reflectivity decreases after the first pulse, but further pulses produce no significant changes. From the above assumed reflectivity values for a- and c-$Si_{0.8}Ge_{0.2}$, a reflectivity decrease of 20% for an $a \rightarrow c$ phase change is expected, which is indeed the reflectivity change observed after the first pulse. Therefore, from the data in Fig. 1 we can conclude that after the first pulse c-$Si_{0.8}Ge_{0.2}$ has been formed, through the melting of the film, and that no significant changes affecting its optical properties occur upon further irradiation. Finally, the melt duration measured from the transients shows a constant value around 30 ns in all cases. Since the Ge liquid-phase diffusivity in Si is 2.5×10^{-4} cm^2/s,[21,22] from the measured melt duration it follows that complete diffusion of the Ge into the neighbor Si layers can take place after a single pulse, and a homogeneous alloy can be formed.

Figure 2 shows the RBS channeling and random spectra for a sample grown by PLD and irradiated with four laser pulses. The random spectrum overlaps with that measured for an as-deposited film, indicating that neither has there been loss of material from the surface, nor has there been diffusion of Ge into the underlying Si substrate. The yield observed between 1.2 and 1.4 MeV corresponds to the Ge atoms in the $Si_{0.8}Ge_{0.2}$ film. The channeling spectrum shows a lower yield than the one corresponding to the random thus evidencing heteroepitaxial growth. Therefore, when melting of the film occurs fully in depth, as shown by the maximum reflectivity transient, then solidification starts from the single-crystal seed provided by the Si substrate, and leads to heteroepitaxial growth. In order to estimate the crystalline quality of the film we have measured the integrated channeled to random yield ratio, for the Ge part of the spectrum ($\chi_{Ge} = y_{chan}/y_{rand}$), this value is related to the percentage of Ge atoms not located in ordered positions with respect to the substrate lattice. Figure 3 shows the χ_{Ge} as a function of the number of accumulated pulses. It can be seen that the best

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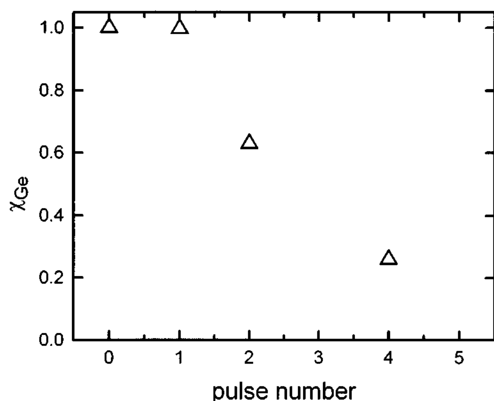

FIG. 3. Integrated channeled to random yield ratio for the Ge part of the spectrum ($\chi_{Ge} = y_{chan}/y_{rand}$) as a function of the accumulated number of pulses, and determined from the RBS/channeling measurements.

channeling is achieved for samples irradiated with at least 4 pulses. Nevertheless, the real time reflectivity measurements show that two pulses are enough to achieve crystallization. These results suggest that the first pulse is indeed enough to induce crystallization of the film, the role of the subsequent pulses being to improve the epitaxial quality of the films. The lack of sensitivity of the transient reflectivity measurements to the later process can be explained by the increase of the probe penetration depth once crystallization takes place. The $1/e$ penetration depth of the HeNe wavelength changes from 60 nm for *a*-Si to 2.5 μm for *c*-Si.[18,19] Since the values for *a*- and *c*-$Si_{0.8}Ge_{0.2}$ should be very similar to the corresponding ones for Si, it becomes clear that the fraction of the probed volume related to the $Si_{0.8}Ge_{0.2}$ 30 nm film becomes smaller once crystallization is achieved.

The χ_{Ge} after 4 pulses reaches a value (25%) that may seem quite high. Nevertheless, this value includes the contribution of the surface disorder, which cannot be separated from the film, due to its small thickness and our experimental resolution. The corresponding χ_{min} for the Si part of the spectrum only reaches a value of 13%, pointing out that the presence of defects in the heteroepitaxial $Si_{0.8}Ge_{0.2}$ film is most likely. Previous results of pulsed laser assisted epitaxy induced in *e*-beam deposited $Si_{1-x}Ge_x$ alloys show that films with $x>0.19$ have a moderate density of dislocations.[4] The origin of these defective structures is still a subject of controversy. They were initially attributed to solute (Ge) partitioning at the solid–liquid interface during solidification, leading to interface instabilities via constitutional supercooling.[4,23] Very recent experiments have confirmed and quantified Ge segregation during pulsed laser assisted heteroepitaxial growth.[21,22] However, for the present experimental conditions our RBS measurements are not sensitive to Ge segregation. Besides, calculations based in an extended stability model show that the rates at which these instabilities develop are too slow to destabilize the interface in a ns time scale.[21]

In conclusion, we have shown that heteroepitaxial $Si_{0.8}Ge_{0.2}$ films can be grown on Si(100) at room temperature by an all-laser-assisted process performed with ArF laser radiation: alternate pulsed laser deposition of amorphous Si and Ge, followed by laser induced melting, diffusion, and solidification. We have also shown that PLD can be performed from two independent targets, thus easily allowing the growth of alloys in a wide range of compositions and avoiding the need of specifically designed targets.

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