Low-temperature solid-phase heteroepitaxial growth of Ge-rich Si_xGe_{1-x} alloys on Si (100) by thermal annealing *a*-Ge/Au bilayers

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Heteroepitaxial layers of Si_xGe_{1-x} alloys were grown on Si(100) by thermal annealing bilayers of *a*-Ge/Au deposited on single-crystal Si (sc-Si) substrates at 300 °C. During annealing, Ge dissolves into the Au layer and then grows epitaxially to the substrate, with the final structure changing from *a*-Ge/Au/sc-Si to Au/Si_xGe_{1-x}/sc-Si. The Si_xGe_{1-x} layer was found to be Ge rich ($x \approx 0.15$) from AES and STEM analysis and to be epitaxial to the Si(100) substrate from the x-ray rocking curve and RBS channeling measurements. Stacking faults and microtwins are the major defects in the epitaxial film, as observed by cross-sectional TEM. High-resolution TEM analysis of the Si_xGe_{1-x}/Si interface shows that the growth initiates at specific areas of the original Au/Si interface. This work demonstrates for the first time both heteroepitaxial growth and the growth of Si_xGe_{1-x} alloys on Si(100) using solid phase epitaxy with an eutectic-forming metal as the transport medium.

Continuous progress in the fabrication of high-speed heterojunction devices based upon narrow band-gap epitaxial Si_xGe_{1-x} layers on Si[1,2] has stimulated different techniques for growing low defect density epitaxial Si_xGe_{1-x} alloys on Si(100) substrate. In addition, like GaAs on Si, growth of high-quality Ge-rich Si_xGe_{1-x} epitaxial film on Si substrate is of scientific interest for fundamental understanding of the growth mechanism due to large lattice mismatch (up to 4.1% for pure Ge on Si) in this system. Such large lattice misfit has resulted in unacceptably high defect densities in the epitaxial films, especially threading dislocations.[3] Most of the research in the growth study has been focused on four growth techniques, i.e., molecular beam epitaxy (MBE), rapid thermal chemical vapor deposition (RTCVD), ultrahigh vacuum chemical vapor deposition (UHVCVD), and recently developed pulsed laser-assisted deposition. Although each of these deposition techniques have demonstrated growth of fairly good epitaxial films, the cost and limitations of each method are still the main concerns.[4–7]

As an alternative growth method, solid-phase epitaxial (SPE) growth with an eutectic-forming metal as the transport medium is a low-temperature process with great flexibility for selective growth and conformal growth. This has been demonstrated in our previous work on recrystallization of polycrystalline Si on patterned Si substrate via Au medium.[8,9] The SPE process is accomplished during post-deposition anneal of a sample with the metal layer between the amorphous semiconductor and single-crystal substrate. The role of the metal is to enhance the mobility of diffusing species, to provide a short diffusion path without forming compounds with the diffusing species, and also to confine the shape of growing crystal. There are two thermodynamic driving forces in this process: (1) the reduction in the Gibbs-free energy associated with the amorphous-to-crystalline transition; and (2) the reduction in interfacial energy between the metal/amorphous layer interface and the newly generated crystalline layer/substrate interface. To date, this technique has only been employed for solid-phase homoepitaxy of amorphous film over the same single-crystal (sc) substrate in a few systems such as *a*-Si/Al/sc-Si, *a*-Ge/Al/sc-Ge.[10]

In this letter, we present our preliminary studies on low-temperature growth of epitaxial Ge-rich Si_xGe_{1-x} alloys on Si(100) substrate using solid-phase epitaxial (SPE) growth technique. In this work, Au was selected as a transport medium due to the similar low eutectic temperatures formed on both Au-Ge and Au-Si systems, which are 361 ° and 363 °C, respectively.[11] To the best of our knowledge, this work demonstrates for the first time low-temperature SPE growth of a heteroepitaxial structure. It also represents the first time that a Si_xGe_{1-x} alloy has been grown on Si(100) using the SPE growth technique.[12] The results show that the SPE process using Au metal medium has a feature of conformal growth and is a promising low-temperature growth method with potential applications for selective growth of Si_xGe_{1-x} epitaxial films on patterned Si substrate and the growth of SOS structure.

The substrates used in this study were *p*-type, boron-doped Si(100) wafers. The wafers were first degreased and then chemically cleaned by dipping in a diluted ($HF:H_2O = 1:50$) HF solution just prior to loading into a thermal evaporation system with a base pressure of 2×10^{-6} Torr. A 1450-Å-thick Au film was deposited onto the Si substrate as a first layer, then an amorphous Ge layer of 1420 Å in thickness was sequentially evaporated onto the Au layer without breaking the vacuum. The deposition rates of both Au and *a*-Ge were about 30 Å/s. The pressure was maintained at 5×10^{-6} Torr during evaporation. The samples were subsequently annealed in high vacuum (10^{-8} Torr) at temperatures in a range from 280° to 310 °C using a conventional tube furnace. Upon annealing the sheet resistance was measured *in situ* to monitor the progress of the amorphous-to-crystalline phase transition. After annealing, the samples were characterized for epitaxial quality and composition using x-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS) and ion channeling, Auger electron spectroscopy (AES), and

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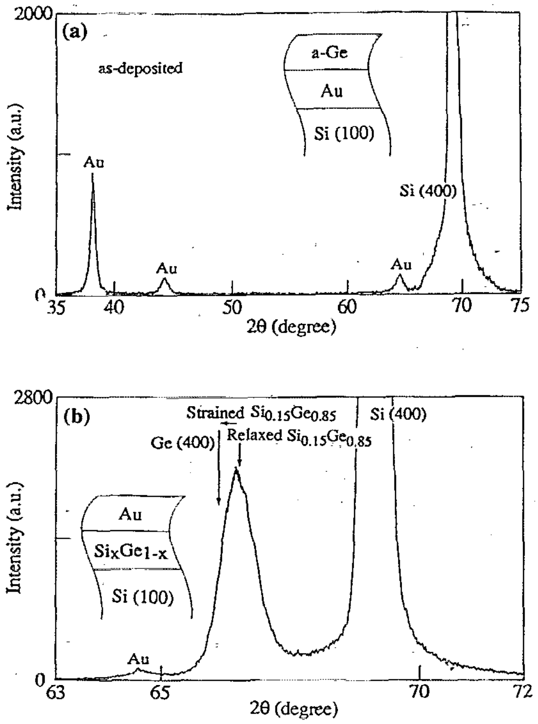

FIG. 1. X-ray diffraction spectra for (a) as-deposited sample and (b) sample annealed at 300 °C for 30 min.

cross-sectional transmission electron microscopy (XTEM). Also, the samples were analyzed for composition uniformity inside the epitaxial Si_xGe_{1-x} film using scanning transmission electron microscopy (STEM) with a probe size of 10 Å.

Figure 1 shows x-ray diffraction spectra for samples before and after thermal annealing. Prior to annealing, x-ray diffraction measurements indicate that the as-deposited Ge film was amorphous (absence of Ge peaks) and the Au film polycrystalline. After an anneal at 300 °C for 30 min, one additional peak is observed on the left of the Si(400) peak [Fig. 1(b)]. A closer look of the position of the peak suggests that this additional peak corresponds to a Ge-rich Si_xGe_{1-x} alloy.

In order to ascertain the orientation relationship between the Si_xGe_{1-x} film and the Si substrate, x-ray rocking curve measurement was performed on the film. The result shows that the Si_xGe_{1-x} film is epitaxial to the Si substrate with the full width at half maximum (FWHM) of about 2160 s, as shown in Fig. 2.

The annealed samples were also examined by cross-sectional transmission electron microscopy (XTEM). A low-magnification XTEM micrograph for a sample annealed at 300 °C is shown in Fig. 3. As seen in the micrograph, the interface between the epitaxial Si_xGe_{1-x} film and Si substrate is clearly visible due to the remaining native oxide at the original polycrystalline Au/Si interface. The thickness of the Si_xGe_{1-x} film is about 1450 Å. This is essentially equal to the original thickness of the Au layer. The Au layer is observed on the top of the epitaxial film, replacing the position of the original amorphous Ge layer. Inside the Si_xGe_{1-x} film close to the Si_xGe_{1-x}/Si interface, we see a small amount of Au has been trapped in the layer, as indicated by arrows in the XTEM micrograph. Electron diffraction also confirms that the Si_xGe_{1-x} film is epitaxial with the Si substrate. However, we also observe structural defects inside the Si_xGe_{1-x} film. Close examinations of the film by TEM show that the major defects in the film are stacking faults and microtwins, and no threading dislocations were seen in several identical samples. The voidlike features seen in the epitaxial film are believed to be real voids originally formed in the evaporated Au film.[13]

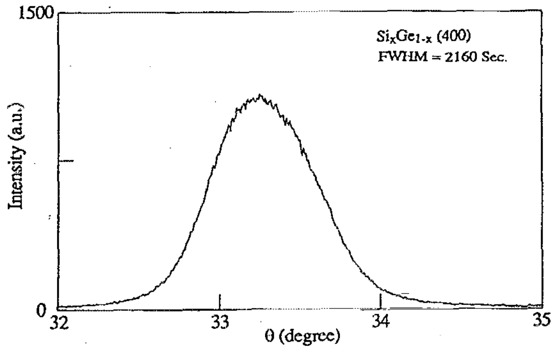

FIG. 2. X-ray rocking curve of epitaxial Si_xGe_{1-x} film grown on Si(100) substrate after annealing at 300 °C using solid phase epitaxy. FWHM ≈2160 s.

To obtain the information of composition and uniformity of the epitaxial Si_xGe_{1-x} film, we used scanning transmission electron microscopy (STEM) with a probe size of 10 Å to obtain local composition of the small features inside the film. And also, we used commercially available Au etchant (type TFA)[14] to remove the surface Au layer. The samples after removal of surface Au were reanalyzed using AES, RBS, and ion channeling. The results from STEM and Auger depth profiling show that the average composition of the epitaxial Si_xGe_{1-x} film is $x=0.15\pm0.02$. Based upon this composition information, the x-ray (400) peak

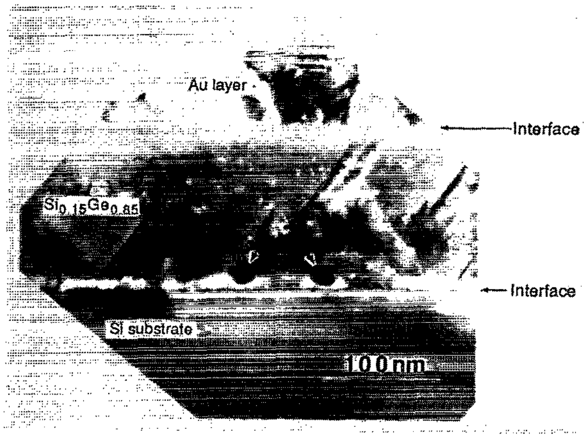

FIG. 3. Cross-sectional TEM micrograph of a sample annealed at 300 °C for 30 mins. The white contrast at the Si_xGe_{1-x}/Si interface is due to remaining native oxide. Au layer is observed on the surface. Also small amount of Au has been trapped in the Si_xGe_{1-x} film close to the original Au/Si interface, as indicated by arrows.

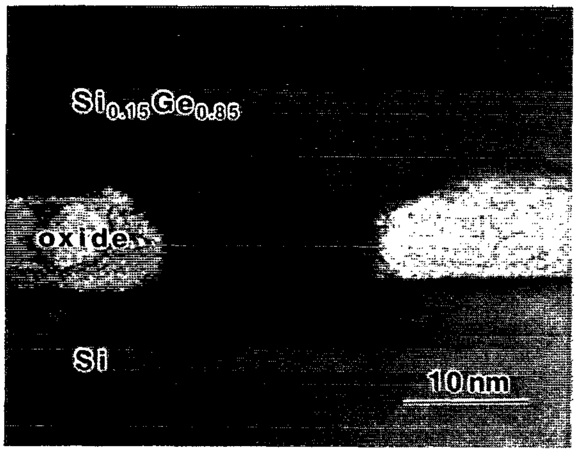

FIG. 4. High-resolution cross-sectional TEM micrograph for a sample presented in Fig. 3, showing interfacial structure between Si_xGe_{1-x} film and Si substrate. The white contrast is due to remaining native oxide, some of which are behind Si_xGe_{1-x} film. The black contrast shown at the interface implies that the epitaxial film is strained.

corresponding to $Si_{0.15}Ge_{0.85}$ film should appear at the position indicated by an arrow in Fig. 1(b) if the epitaxial film was relaxed. The difference between XRD and STEM, AES measurements suggests that the epitaxial film may be slightly strained. STEM analysis of several voidlike features does not reveal any Au signals except for Ge, Si, and a small signal of Cu. No difference in composition was seen between the film and void-like features. This seems to support our previous suggestion of voids. RBS results after removal of the surface Au layer reveal that there is only a small amount of Au at the original Au/Si interface of the sample. This picture is consistent with our TEM observations.

RBS channeling after the removal of Au also confirms that the Si_xGe_{1-x} film is epitaxial on the Si substrate with χ_{min} (channeling minimum yield) $\approx 54\%$. The dechanneling is thought to be partially due to the structural defects in the epitaxial film.

The interface between the epitaxial film and Si substrate was further examined by high-resolution cross-sectional transmission electron microscopy (HRXTEM). A typical micrograph showing interfacial structures is presented in Fig. 4. We see that the Si_xGe_{1-x} film has very good lattice registry with the underlying Si substrate. Microtwin is also seen inside the Si_xGe_{1-x} film. The black contrast exhibited at the interface between epitaxial film and Si substrate also implies that the epitaxial Si_xGe_{1-x} film is strained. It is surprising that the film extends the epitaxial feature laterally even over the intervening native oxide (the regions with white contrast were qualitatively identified as silicon dioxide using an EDS windowless technique), which is about 60 ~ 100-Å thick.

With respect to the growth process, we believe that the original Au/Si interface is not laterally uniform but consists of two different types of interfaces: one with native oxides in between ($Au/SiO_2/Si$) and the other without intervening oxides (Au/Si). The growth initiates at certain Au/Si interfaces without intervening oxide by diffusion of Ge atoms through the Au transport medium and the incorporation of Si in the film. The dissolution of Si from certain areas of the Si substrate into Au and the migration of Ge atoms through the Au transport medium may occur concurrently. Ge atoms diffuse through the Au layer and attach epitaxially onto the Si substrate, simultaneously incorporating a small amount of Si dissolved in Au. As growth proceeds, Au is gradually displaced due to the simple eutectic natures of Au-Ge and Au-Si systems. Obviously more knowledge concerning the controllability of Si incorporation and understanding of the dynamic picture of the growth of Si_xGe_{1-x} alloys on Si substrate using the SPE growth technique is needed.

In conclusion, we have demonstrated for the first time that Ge-rich Si_xGe_{1-x} alloys can be heteroepitaxially grown on Si(100) substrate using a low-temperature SPE growth technique with Au as the transport medium. The growth process proceeds at temperatures well below the eutectic points for either Au-Ge or Au-Si and exhibits good selectivity and conformability. The film grown on Si(100) in this way has stacking faults and microtwins but no threading dislocations.

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