Low-temperature homoepitaxial growth on Si(111) mediated by thin overlayers of Au

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High quality homoepitaxial growth of Si on Si(111) through an overlayer of Au is shown to occur at 450–500 °C, far below the temperature required for growth of Si of similar quality on bare Si(111). Films of unlimited thickness can be obtained with excellent crystalline quality, as revealed by Rutherford backscattering spectrometry ion channeling measurements (χ_{min}=2.2%). A distinct range of Au coverage (0.4–1.0 monolayer) results in the best quality epitaxy, with no measurable amount of Au trapped at either the interface or within the grown films. Cross-sectional transmission electron microscopy reveals that in films grown with Au coverages below and above the optimum range, the predominant defects are twins on (111) planes and Au inclusions, respectively.

Single crystal growth of semiconductors through surface mediating layers has been studied extensively in recent years. Wagner and Ellis first demonstrated metal-mediated crystal growth at 950 °C through the vapor-liquid-solid (VLS) growth mechanism for semiconductors.[1,2] VLS growth occurs through a thick, liquid eutectic layer, by transport of atoms from the vapor followed by their attachment to the solid substrate. In the first experiments, large-area planar growth could not be achieved because of insufficiently clean and homogeneous surface conditions. With improved vacuum technology and hence surface cleanliness, growth of high quality, planar films became possible.[3] Overlayer thicknesses have since been minimized so that transport through the mediating layer is not the limiting step in the growth mechanism. Several researchers have shown that mediating overlayers[4] can be used to improve homoepitaxial and heteroepitaxial growth of Si and Ge.[5–9] These studies, however, have been limited to growth of very thin epitaxial layers [1–50 monolayers (ML), where 1 ML=7.84×10^{14} cm^{-2} on Si(111)], and this offers only a limited study of the microstructure. Iwanari *et al.*[5] have shown homoepitaxy of Si on Si(111) through a Sn layer at 330–420 °C, by observing growth of the first few monolayers with reflection high-energy electron diffraction and reflection electron microscopy. While these techniques are important for determining step flow and island nucleation on the Si surface during initial stages of growth, they cannot be used for analysis beyond the first few layers. It is desirable to be able to grow much thicker layers, so that the microstructure of the grown films can be studied on a larger scale.

Homoepitaxial growth on Si(111) is inherently difficult at low temperatures. Typically, the substrate must be held above 700 °C[10] during deposition to obtain high quality films of unlimited thickness. Weir *et al.*[11] have demonstrated homoepitaxial growth on bare Si(111) for limited thicknesses, at deposition rates of 0.1–3.0 Å/s, and corresponding growth temperatures of 380–450 °C. The films were about 350 Å thick, and the epitaxial quality deteriorated rapidly with distance from the initial interface. Buffer layers predeposited at 700 °C were necessary to obtain clean substrate surfaces.

In this study we present a systematic investigation of Au coverages on the Si(111) surface which act as mediating layers in the epitaxial growth of Si films. We show that there exists a narrow optimum range of Au coverages which produces grown films of excellent crystalline quality at low temperature, and leaves none of the surface Au trapped in the film. The films were grown without a predeposited buffer layer. We have grown epitaxial films up to 5000 Å thick, and there are no indications of a limit to the thickness for films grown by our technique. Films grown over large planar areas in this manner, with surface overlayers of Au, are important because of their potential use in device fabrication. We also discuss the effect of temperature on the crystalline quality of the epitaxial layers grown at various deposition rates, and analyze the resulting morphology of the films.

Samples were obtained from 3 in. *p*-type wafers, with ρ=0.02–0.08 Ω cm, and a miscut angle of 2.63°±0.15°. All samples were etched using the Shiraki procedure,[12] then heated *in situ* at 900 °C by direct current through the sample for 5 min under ultrahigh vacuum (UHV) conditions. The depositions were done in an UHV chamber, with base pressure 7.0×10^{-11} Torr. The substrate temperatures in this experiment ranged from 375 to 500 °C, and were measured with an optical pyrometer. The pyrometer measurements agreed to ±5 °C with thermocouple calibration measurements over the temperature range used in this experiment. Au was deposited on atomically clean, 7×7 reconstructed substrate surfaces from a standard effusion cell; Si was then deposited by electron beam evaporation. In all cases the Au was deposited (at less than 0.1 Å/s) at the same substrate temperature as the Si. The deposition rates of Si were varied between 0.5 and 3.0 Å/s, as determined by a quartz crystal monitor [calibrated by Rutherford backscattering spectrometry (RBS)]. Low-energy electron diffraction (LEED) was used to monitor the surface reconstruction after the Au deposition, as well as after the Si deposition. The samples were masked so that only half of the surface was covered by Au. In all samples Si was deposited over the entire surface, so that direct comparison could be made between regions with Au and regions without Au under otherwise identical conditions. Pressures during Si deposition were lower than 5.0×10^{-9} Torr. After epitaxial growth, the samples were analyzed *in situ* by RBS (2 MeV $^4He^+$) and channeling. Some samples were analyzed *ex situ* in a separate beam line for

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glancing angle analysis. Oxidation during sample transfer caused no measureable change in the RBS spectra of the grown films. After RBS, most of the samples were studied by cross-sectional transmission electron microscopy (TEM).

Substrate temperature, Au coverage, and Si deposition rate were varied in this experiment in order to determine the effect of these parameters on the epitaxial quality of the film. Varying the Si deposition rate between 0.5 and 3.0 Å/s had no observable effect on the quality of the films. This result is significant, since it differs from that for deposition on bare substrates, where the film quality depends strongly on deposition rate.[11] Au coverages ranged from 0.15 to 3.0 ML, and we found from LEED and RBS that the Au coverages and corresponding surface reconstructions before and after Si deposition at 375–500 °C were the following: mixed 5×1 and 7×7 for Au less than 0.4 ML, mixed 5×1 and $\sqrt{3}\times\sqrt{3}$ for Au between 0.4 and 0.8 ML, only $\sqrt{3}\times\sqrt{3}$ (or 6×6, above 1 ML) for Au above 0.8 ML. This is in agreement with previous observations,[13] which used LEED and scanning tunneling microscopy. Before Si deposition, several samples were annealed at 750 °C for 1 min immediately following Au deposition. The annealing caused no measurable change in the resulting epitaxial quality of the grown films.

Figure 1 shows four sets of RBS and channeling data under direct backscattering conditions for films grown at 450 °C. Figure 1(a) shows spectra for growth of 1400 Å Si on bare Si(111). The high energy portion of the spectrum shows that no Au was deposited. The aligned spectrum has a relatively large χ_{min}=30%, which indicates that the film is highly defective. Figure 1(b) shows the spectrum for a 1700 Å film grown under the same conditions as (a), except that 0.15 ML of Au was deposited prior to the Si deposition. This results in a drastic improvement in the aligned yield (χ_{min}=10%). Figure 1(c) shows the random and aligned spectra of a 1000 Å film grown with an Au coverage of 1.0 ML. It has the best quality of any of the films grown at

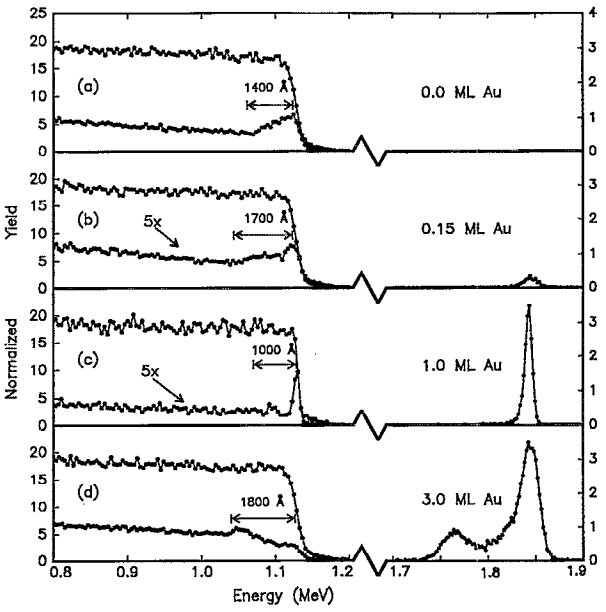

FIG. 1. RBS random and aligned spectra of Si grown on Si(111) through overlayers of different thickness; all substrates were at 450 °C. The normalized counts for the Au peaks at high energy are on the right axis. (a) 1400 Å Si film grown with no (0.0 ML) Au. (b) 1700 Å Si film grown with 0.15 ML of Au. (c) 1000 Å Si film grown with 1.0 ML of Au; the aligned yields in both (b) and (c) have been multiplied by a factor of 5 in order to show detail in the spectra. (d) 1800 Å Si film grown through 3.0 ML Au with a large amount of Au trapped in the film.

450 °C, as the aligned yield (χ_{min}=2.4%) is nearly equal to that of a bare Si wafer. The channeling yields in Figs. 1(b) and 1(c) have been multiplied by a factor of 5 in order to show detail. Further, all of the Au remains at the surface of the film in both Figs. 1(b) and 1(c); no Au is detected at the substrate interface or in the grown film, as can be seen from the Au peak at high energy. Figure 1(d) shows the aligned

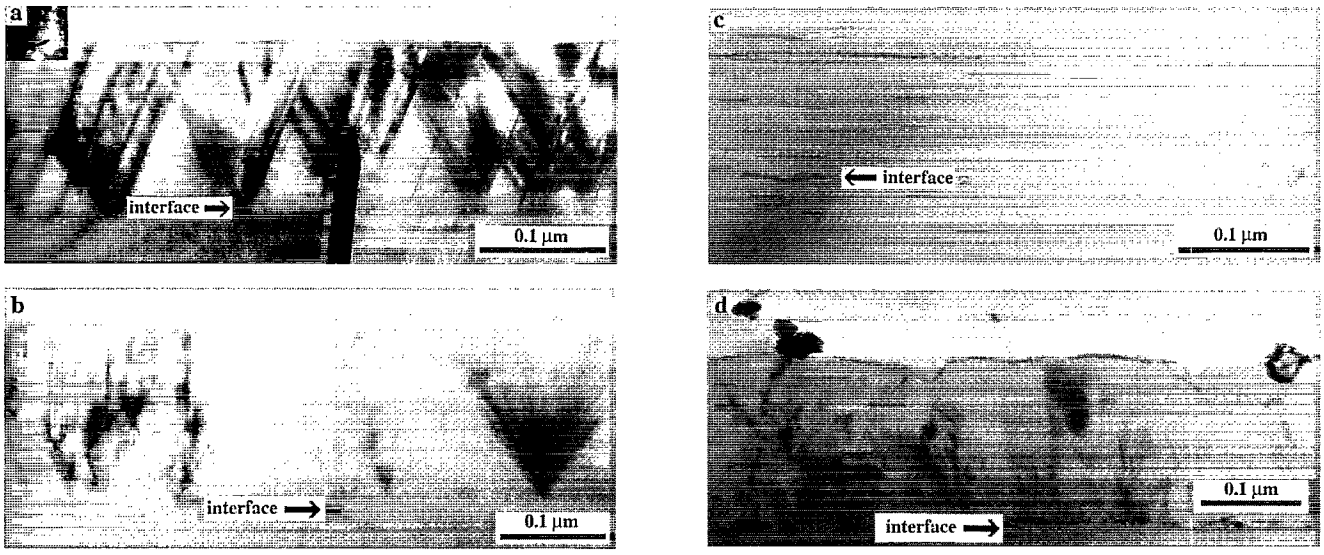

FIG. 2. Transmission electron micrographs of the samples in Fig. 1 (grown at 450 °C). (a) Highly defective film grown with no Au on the substrate surface, (b) slightly defective film [mostly twins on (111) planes] grown through 0.15 ML Au, (c) nearly perfect crystal, showing no defects or Au trapped in film. (d) Large Au inclusions are on the film surface and trapped within the layer.

spectrum for a 1800 Å film grown with 3.0 ML Au. The epitaxial quality of the film is far worse than for 1.0 ML Au, because about 1 ML (7.7×10^{14} cm^{-2} measured) of Au was trapped at the interface and in the grown layer.

Figure 2 shows cross-sectional TEM micrographs of the corresponding samples in Fig. 1, all grown at 450 °C. Figure 2(a) shows a Si film grown with no Au. The 1400 Å film is highly defective, mostly from twins on (111) planes. The twins originate from the substrate interface, and extend to the film surface. The inset figure shows an electron diffraction pattern (⟨110⟩ beam direction) of the same region, with the streaks indicating twins on (111) planes. Two-dimensional nucleation at the initial interface appears to preclude good epitaxial growth from the onset. Figure 2(b) shows a 1700 Å Si film grown with 0.15 ML Au. While the film is much less defective than that of Fig. 2(a), the predominant defects are still twins on (111) planes. It appears that at coverages in this range, there is enough Au to facilitate high quality epitaxial growth in certain regions, but a substantial number of twins are still found in other regions. It should be noted, however, that substantial twinning does not begin at the initial interface: TEM shows that there is about 300 Å of good epitaxial growth before significant twinning begins, and the aligned spectrum [Fig. 1(b)] showed no distinction between this layer and the substrate. Development of a nonuniform distribution of Au on the surface during growth may be the cause of the increased nucleation of twins.

Figure 2(c) shows a micrograph of a 1000 Å Si epitaxial layer grown with 1.0 ML Au. The grown layer is nearly defect free throughout the entire film thickness. The Au coverage is close to optimal and allows nearly perfect epitaxial growth, with no excess Au trapped in the film. For all Au coverages within the range 0.4–1.0 ML, the crystalline quality is excellent. The quality of films grown with Au coverages outside this range is much lower, as shown in Fig. 2(d), which shows a micrograph of a 1800 Å Si film grown at 450 °C on 3.0 ML Au. It can be seen that for coverages above about 1 ML, epitaxial growth still occurs, but that a large amount of Au is trapped both at the interface and in the grown layer.

Figure 3 is a plot of χ_{min} as a function of Au coverage and temperature, at deposition rates of about 3 Å/s. The graph clearly shows that χ_{min} is lowest for Au coverages between 0.4 and 1.0 ML. Above about 1.0 ML, a higher χ_{min} results from dechanneling by Au trapped within the film. It can be seen that above 450 °C and with Au coverages in the optimum range, χ_{min} is within a few percent of that for a bare Si wafer (χ_{min}=2.2%). At 500 °C, χ_{min}=2.2% for Au between 0.8 and 1.0 ML. The epitaxial quality of the films quickly deteriorates outside of this range, for reasons already discussed. Further, Fig. 3 shows that a temperatures as low as 410 °C, epitaxial films (χ_{min}=14%) can be grown with an Au coverage in the optimum range, even though Si grown without Au (0.0 ML) is extremely defective. At 375 °C, however, even films grown with Au are highly defective. The overall trend shows that the film quality improves with increasing temperature, and that defect-free films can be produced at temperatures as low as 450 °C; without Au, similar quality can only be obtained above 700 °C.[10]

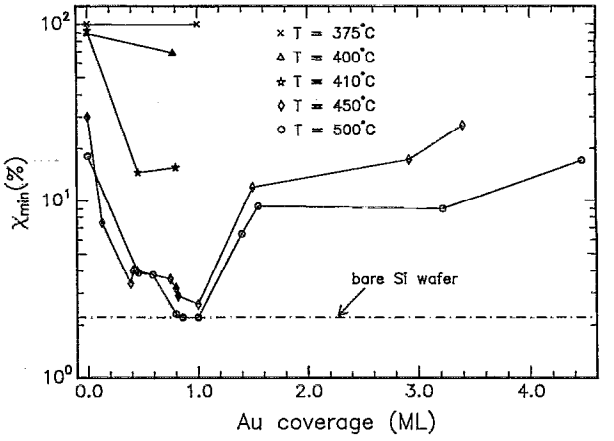

FIG. 3. Plot of χ_{min} vs Au coverage at several temperatures, for a deposition rate of 3 Å/s. At temperatures below 410 °C, Si films grown with or without Au are extremely defective. Above 450 °C, Au coverages between 0.4 and 1.0 ML results in high quality epitaxial films.

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