

Liquid-metal-mediated homoepitaxial film growth of Ge at low temperature

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We demonstrate liquid-metal-mediated homoepitaxial crystal growth of Ge on Ge(111) at temperatures in the range of 400–450 °C. Crystal growth proceeds by diffusion of Ge through a liquid layer, followed by precipitation onto the substrate by the vapor-liquid-solid mechanism. The liquid-metal phase at the interface is a Au-Ge alloy formed by initial deposition of a thin Au layer above the eutectic temperature. Ge vapor is provided by a molecular-beam evaporator. The resulting films revealed high-crystalline quality by *in situ* high-energy ion scattering and channeling analysis and *ex situ* by cross-sectional transmission electron microscopy.

It has been known for years that the presence of certain metals on a solid semiconductor surface greatly enhances the crystal growth rate. Growth of Si crystals by the vapor-liquid-solid (VLS) mechanism using Au was demonstrated in 1964 by Wagner and Ellis.^{1,2} They suggested that the metal formed a liquid solution with the semiconductor, and that crystal growth occurred by precipitation of the semiconductor atoms from the supersaturated liquid at the liquid-solid interface. The concentration gradient across the metal solution was the driving force for diffusion of the semiconductor atoms from the surface to the interface. Crystals resulting from this process usually were long, dislocation-free whiskers or filamentary protrusions. The VLS process was not converted into a reliable planar technology, partly because the substrates did not have a clear surface and well-defined and homogeneous properties.

A similar process, solid-phase epitaxial (SPE) growth with metals as transport media, has been much more extensively studied in recent years.^{3–5} In the SPE process, samples are prepared with a metal layer separating an amorphous semiconductor layer from the crystalline semiconductor substrate. Upon annealing well below the eutectic melting temperature, the atoms from the amorphous layer migrate through the metal layer and attach epitaxially onto the substrate. The driving force for the SPE process is the reduction in the free energy associated with the amorphous-to-crystalline transition. The substrate-metal interfaces again play an important role in the quality of the grown crystal; the epitaxial layer grown in this way generally lacks lateral uniformity and good crystal perfection if contamination and inhomogeneity is present at the interface.^{3,4}

We have undertaken an investigation of the homoepitaxial growth of crystalline semiconductor films by the VLS mechanism in the context of modern surface preparation and diagnosis techniques.⁶ Our method is very similar to that of Wagner and Ellis^{1,2} for VLS crystal growth of Si with Au transport medium, except that we use a purified molecular-beam source instead of a chemical compound vapor. This eliminates many problems, including

the high temperature (800–900 °C) required to decompose the vapor compound, and possible contamination of the growing layer. Another important difference is that we deposited the metal, atom by atom, on a hot and atomically clean surface, ensuring uniform mixing of the metal and the semiconductor material at the first stage of the process, promoting two-dimensional film growth. Our aim is to explore a new potential method for large-area device-quality thin-film growth or for patterned growth of semiconductors at low temperature. Ge homoepitaxial growth on Ge(111) has been successfully demonstrated with a Au metal medium at temperatures in the range of 400–450 °C. We have found that the liquid-metal medium greatly enhances the quality of the films grown at these low temperatures.

The experiment was carried out in an ultrahigh vacuum (UHV) system, equipped with a low-energy ion gun, effusion cells, and low-energy electron diffraction (LEED) optics. The UHV chamber was also connected to a General Ionex 1.7-MV Tandem accelerator in order to perform Rutherford backscattering (RBS) and channeling RBS (CRBS) analysis. These instruments provide material deposition, as well as *in situ* growth process diagnosis and sample characterization. The sample was heated resistively by passing a current through them. An optical pyrometer was used to measure the temperature. The base pressure of the chamber was 1×10^{-10} Torr and was kept within the 10^{-10} Torr range during sample preparation and growth.

The substrates used in this study were *p*-type, low-resistivity (0.01 Ω cm), surface mirror-smooth polished Ge(111) wafers. A clean substrate surface was first prepared inside the UHV chamber by alternate low-energy Ar-ion sputtering and annealing at 650 °C until a $c(2 \times 8)$ LEED pattern was consistently observed. A thin metal Au layer was then deposited on this surface either by ion sputtering from a solid Au target or by evaporation from an effusion cell. During the Au deposition, the substrate was kept at 400 °C, so that the Au and Ge form a eutectic melt which has an eutectic composition of 72 at. % Au at a temperature of 361 °C.⁷ To minimize Au island formation due to phase separation, the substrate was kept above the eutectic temperature after the Au deposition. The Ge for VLS growth was provided by a molecular beam from an

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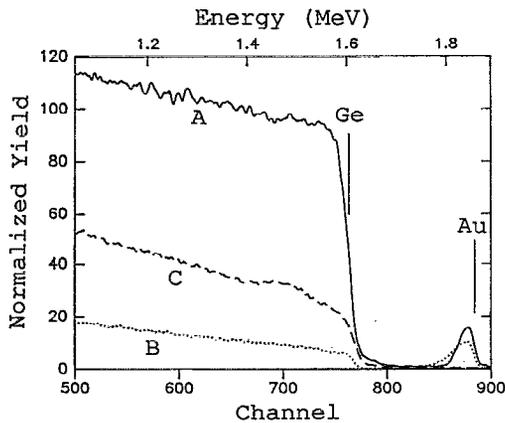


FIG. 1. RBS spectra of a sample with deposition of 1000 Å Ge/16 Å Au-Ge on Ge(111) at 425 °C: (A) random RBS before Ge deposition, (B) channeling RBS after Ge deposition. (C) CRBS spectrum of a sample with deposition of 2800 Å Ge on Ge(111) at 400 °C, but without Au medium.

effusion cell. The cell was placed 10 cm away from the substrate, and operated at 1200–1300 °C, resulting in an evaporation rate of 10–25 Å/min. After the Ge deposition, the temperature was checked, and had typically risen 5–10 °C. The sample was kept at the growth temperature for an additional 20 min, then cooled down slowly.

Figure 1 shows the resulting spectra of ion scattering and channeling measurements, where 2-MeV He ions were incident along the sample normal with the solid-state detector set at 170° to the ion incident direction. Curve A is a random RBS spectrum from a sample after Au was deposited, but before Ge deposition. Integration of the Au peak shows that this sample had 7.1×10^{15} atoms/cm² of Au, corresponding to 16 Å of 3:1 Au-Ge eutectic. By analyzing the shape of the Au peak, we estimate that 70% of Au formed a flat eutectic layer, and the remaining 30% was balled up in islands. Curve B shows the CRBS spectrum of this sample after 1000-Å Ge deposition at 425 °C. The sample has a low dechanneling yield of less than 8%, indicating that the Ge grew epitaxially on the surface with good crystallinity. An extended tail indicates that a small amount of Au has been trapped in the layer, and that most of the Au is still in a Au-Ge alloy on the surface or in islands on the surface. As a comparison, we show a CRBS spectrum (curve C) from a sample which had 2800 Å Ge grown at 400 °C with no Au layer. The dechanneling yield is much poorer (26%), indicating worse crystal quality. Thus, although it is possible to grow Ge epitaxially at 400 °C without a liquid-metal layer, the presence of metal dramatically improves the quality of the resulting films.

To confirm that most of the Au was still at the surface after the VLS growth, we used selective chemical etching to remove the surface Au. We applied a commercial Au etchant (type TFA)⁸ at room temperature for 3 min, and rechecked the sample by RBS and channeling where 2-MeV He ions were used with a coaxial solid-state detector set at a detection angle of 180°. The resulting spectra from a sample [1500 Å Ge grown through 46 Å of Au-Ge eutectic on Ge(111) at 450 °C] are presented in Fig. 2. Curve

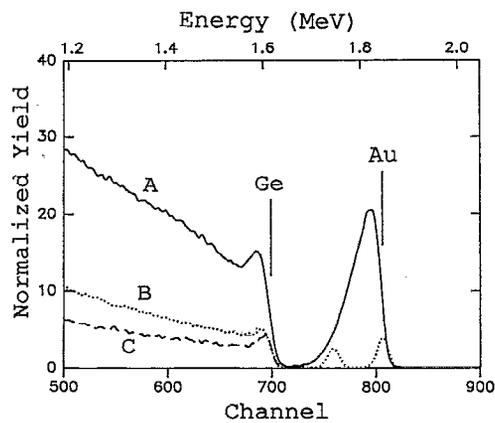


FIG. 2. CRBS spectra of a sample with deposition of 1500 Å Ge/40 Å Au-Ge on Ge(111) at 450 °C: (A) after growth, (B) after surface Au removed by etching. (C) CRBS spectrum of a clear Ge(111) surface.

A is the CRBS spectrum before etching, showing a 14.5% dechanneling yield. Curve B is one from the same sample after etching; the Au signal is present in two small peaks: one (1.5×10^{15} atoms/cm²) at the surface and one (0.9×10^{15} atoms/cm²) at the original interface. The gap between these two peaks corresponds to a 1500-Å-thick epitaxial Ge layer, in agreement with the deposition record. Furthermore, removal of the surface Au improved the dechanneling yield to 4.8%, very close to the ideal of 3.4% observed from a clear Ge(111) surface (curve C). This is because the Au layer at the surface scatters the ion beam strongly off their channeling direction. The formation of Au-Ge islands on the grown sample surface has also been confirmed by scanning electron microscopy (SEM) examination. Figure 3 shows a typical SEM micrograph of a grown sample with Ge(1000 Å) grown through the Au(30-Å) layer on Ge(111) at 400 °C. The islands in sizes of 1000–2000 Å in diameter are observed. Otherwise, the surface is relatively smooth, indicating by the weak contrast background. It is suggested that the islands are formed through recrystallization and phase separation during cooling after the growth process.

We have also examined the grown samples using cross-sectional transmission electron microscopy (XTEM). One XTEM micrograph of a sample is shown in Fig. 4. In this sample the interface between the original substrate and the epitaxial layer is barely visible since this is homoepitaxial growth. The thickness of the epitaxial layer is about 1000 Å. The similarity of the contrast features in these two regions indicates good crystallinity in the epitaxial layer. Electron diffraction shows that it has the same orientation as the substrate. However, we see structural defects inside the film in addition to wavelike features created by ion milling during cross-sectional specimen preparation. In the region of this picture, one 1000-Å Au island is observed, consistent with CRBS and SEM results. The Au have formed a crystalline facet, with Ge underneath and around the Au crystallite. This suggests that the Ge continues to precipitate from the Au-Ge eutectic liquid on the surface when the sample is cooled down. The dark lines at the

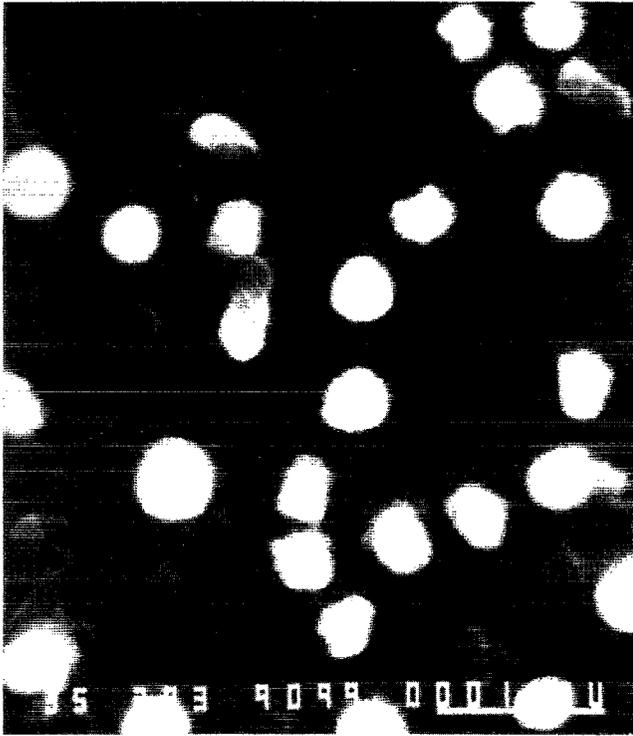


FIG. 3. A typical SEM micrograph from a sample with deposition of Ge(1000 Å)/Au-Ge(30 Å) on Ge(111) at 450 °C. Au islands are observed. Bar = 1 μm.

interface and the surface present in the features correspond to the result shown by CRBS measurements in Fig. 2. There may exist a few monolayers of Au-Ge alloy in these bands. XTEM images of a sample grown without Au show epitaxial growth but with many defects and twin boundaries.

In conclusion, we have demonstrated that uniform crystalline films of Ge can be homoepitaxially grown on Ge(111) by the VLS mechanism using Au in the liquid phase as a transport medium. The growth process proceeds at low temperatures as low as 400 °C, slightly higher than

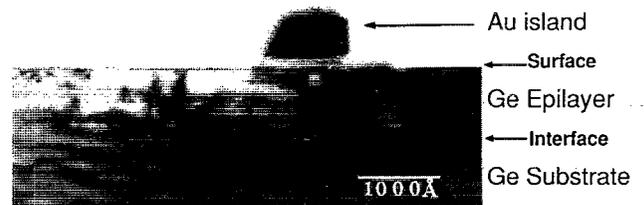


FIG. 4. Cross-sectional TEM micrograph of a sample with deposition of Ge(1000 Å)/Au-Ge(30 Å) on Ge(111) at 450 °C. The interface is seen 1000 Å below the surface, and a 800-Å Au island is observed on the surface. Bar = 1000 Å.

the eutectic point of Au-Ge. The addition of the liquid-metal layer greatly enhances the crystal quality of the grown epitaxial films, and should also permit much higher growth rates. For two-dimensional film growth, the persistence of a flat and uniform Au-Ge liquid layer is essential.

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- ⁸Au etchant (type TFA) is commercially available. It contains KI and I complex, with an etching rate of 2.8 Å/s at room temperature.