Epitaxial growth of amorphous Ge films deposited on single-crystal Ge

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(Received 20 October 1980; accepted for publication 2 December 1980)

The epitaxial growth of amorphous Ge films deposited onto (110) Ge substrate is demonstrated. Substrate cleaning prior to deposition involves only conventional chemical procedures. The growth appears to be a strong function of the interface cleanliness. Two different growth mechanisms are observed: (a) a direct transition from amorphous to single-crystalline layer and (b) the growth involving the transition of amorphous to polycrystals to single crystal.

PACS numbers: 68.55. + b, 68.48. + f, 61.50.Cj, 81.10.Jt

INTRODUCTION

Previous works have shown that in the epitaxial growth of amorphous Si layers deposited on top of a crystalline substrate the cleanliness of the amorphous-crystal interface and the purity of the deposited layers are critical factors. It was found that in samples with surfaces cleaned by chemical methods, the residual interfacial layer causes a delay time t_d in annealing before a detectable epitaxial growth of the deposited Si layer starts. The delay time depends on the thickness of the interfacial layer and on the annealing temperature. Furthermore, an improved epitaxial quality is obtained when the Si is deposited at high rates (~ 50 Å/sec) to minimize the penetration of oxygen in the deposited layer upon unloading of the samples from the vacuum deposition chamber.

In this work we demonstrate the interconnection that exists between the initial interfacial conditions, the delay time for epitaxial growth, and the nucleation time for the formation of polycrystallites during the epitaxial growth of an amorphous Ge layer deposited on single-crystal Ge.

EXPERIMENTAL

Germanium single-crystal substrates, (110) in orientation, were first roughly etched in a 1:4 HF:HNO_3 solution, then oxidized in a 1:40 HF:HNO_3 solution. A final etching was done with a 2% aqueous HF solution to remove the oxide layer. As will be seen later, the sample cleaning procedure is critical and cleaner interfaces were obtained with stronger (~ 10–20%) aqueous HF solution for the final etch.

After etching, the samples were immediately loaded into an evaporation chamber equipped with ion pumps. Amorphous Ge layers ~ 1000-Å thick were evaporated at a rate of ~ 30 Å/sec and a pressure of 7x10^{-7} Torr. The samples were subsequently annealed at temperatures between 400–900 °C in a furnace flushed with forming gas (15 at. % H_2 + 85 at. % N_2 composition). MeV He^+ backscattering spectrometry and channeling effects, x-ray diffraction, and transmission electron microscopy (TEM) were used to investigate the epitaxial growth of the deposited Ge.

All the results shown in this paper were obtained from samples obtained from the same deposition.

RESULTS

Figure 1 shows backscattering spectra obtained with the analyzing beam at random and (110) aligned incidence on samples with ~ 950-Å thick deposited films annealed at 450, 750, and 900 °C for 30, 30, and 10 min, respectively. The spectra taken after 450 °C, 30 min annealing (and after additional annealing at 750 °C, 30 min) show essentially no change in the backscattering yield of the deposited layers, as compared to the random yield, but x-ray diffraction reveals a polycrystalline structure of the deposited layer.

After an initial annealing at 750 °C, 30 min, there is a reduction in the backscattering yield across the deposited layer and the slope in the spectrum corresponding to the back edge of the deposited film indicates the formation of a

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FIG. 1. Backscattering spectra for random and (110) incidence of a 1.5-MeV He^+ beam on a 950-Å-thick amorphous Ge layers deposited onto (110) Ge after annealing at different temperatures.

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FIG. 2. Backscattering spectra obtained with a 1.5-MeV He\(^+\) beam of random and (110) incidence from a 950-Å-thick amorphous Ge on Ge (110) annealed at 750°C for 15, 30, 90, and 225 min showing a progressive reduction of the backscattering yield across the deposited layer for longer annealing time.

A rough substrate-film interface. X-ray diffraction for this sample shows the rings typical of polycrystalline material. These results can be explained in terms of simultaneous presence of epitaxial columns starting from the substrate and polycrystalline grains. After 900°C, 10 min annealing, the near surface minimum yield \(\chi_{\text{min}}\) is about 6% of the random yield. This \(\chi_{\text{min}}\) value is comparable with that obtained from the virgin substrate crystal under the same conditions of analysis (\(\chi_{\text{min}} \sim 6\%\)) and proves that the deposited layer has grown into a single crystal of reasonably good quality. Also, the two spectra show a very similar dechanneling rate indicating that the number of extended residual defects in the deposited layer after annealing at 900°C, 10 min is below the channeling technique sensitivity.

From these results it appears that the structure of the deposited Ge layer is a strong function of the initial annealing temperature and time. To see if the growth depends only on the initial annealing temperature, we performed further annealings at different temperatures on the samples annealed first at 450 and 750°C. No change is observed in the backscattering yield of the deposited layer for the sample initially annealed at 450°C, 30 min after further annealing at 750°C, 30 min, indicating that the polycrystalline structure is stable at this time and temperature (see Fig. 1). The same sample after additional annealing at 900°C, 10 min shows the drop of the backscattering yield across the whole deposited layer, indicating that the polycrystal grains realign themselves with the underlying (110) crystal by growth of epitaxial columns. This last result is easily understood in view of the high annealing temperature (Ge melts at 937°C).

FIG. 3. Transmission electron micrograph of a 950-Å amorphous Ge layer deposited onto (110) Ge after annealing at 750°C for 15 min (upper part) and for 225 min (lower part). The white spots in the micrographs are holes in the films due to the fast etching in the (110) direction during the sample preparation. Diffraction patterns of the same samples are also shown (pictures on right).
The polycrystal realignment phenomenon is observed at lower temperature when the starting material consists of polycrystal grains mixed with some single-crystal columns. We demonstrate this effect in Fig. 2, which shows the backscattering spectra obtained from a sample annealed at 750 °C for 15, 30, 60, and 225 min. The spectra all have the shape characteristic of a rough substrate-layer interface, indicating the laterally nonplanar nature of the crystal growth. A progressive reduction of the backscattering yield across the deposited layer for longer annealing time is observed. X-ray diffraction spectra of this sample shows weakening polycrystalline rings with increasing annealing time. Transmission electron microscopy for the samples annealed at 750 °C for different times shows the simultaneous presence of polycrystalline grains and (110) oriented crystallites. A typical micrograph is shown in Fig. 3 for the sample annealed for 15 min (upper part) and for the sample annealed for 225 min (lower part). The white spots in the micrographs are holes in the film formed by the selectively fast etching in the (110) direction during the TEM sample preparation; some unresolved defects are also present. The diffraction patterns of the two samples also indicate better crystalline quality as annealing time is increased from 15 to 225 min. In fact, in the sample annealed for 225 min a clear single-crystal structure is visible together with very weak polycrystalline rings, while in the sample annealed for 15 min, the presence of polycrystals is quite pronounced. We explain this observation by a lateral growth of the epitaxial columns.

In Fig. 4, the backscattering spectra of a sample annealed first at 750 °C, 30 min and after further annealing at 900 °C, 10 min are shown. In this case also there is a uniform decrease in the backscattering yield across the deposited layer, but the final χmin ~ 15% indicate a worse crystal than the one obtained with direct annealing at 900 °C, 10 min (Fig. 1).

The results presented so far are summarized in Table I. The table shows that the structural characteristics of the deposited layer is not a simple function of the final annealing temperature and time alone. If the first annealing step is at 450 °C, the amorphous layer turns randomly polycrystalline and will remain so even after 30 min of subsequent annealing at 750 °C. An additional annealing at 900 °C for 10 min will prompt the formation of epitaxial columns in the layer. Direct annealing at 900 °C for 10 min, however, leads to a good epitaxial layer. Starting with 750 °C for 30 min forms a mixed layer of randomly oriented polycrystallites and epitaxial columns. These columns grow laterally upon further annealing at 900 °C for 10 min. Obviously, the morphology and mechanism of growth are decided by the temperature of the first annealing and this implies that a double stage annealing will produce a different structure than the one obtained with direct annealing at the higher temperature.

**DISCUSSION**

We believe that our results can be explained in terms of a competition between the delay time $t_d$ for the start of epitaxial growth caused by the nonclean interface between the single-crystal substrate and the deposited layer, and the nucleation time $t_n$ of the polycrystalline grains. It has been shown that for the growth of amorphous Si deposited on Si, the nonclean interface crystal-deposited layer causes a delay time which is a function of the annealing temperature and of the thickness of the interfacial layer before a detectable growth starts. 5

Suppose that (a) the presence of impurities such as O, C, and F slows down the epitaxial growth rate of Ge. A chemi-

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**TABLE I. Summary of the structural characteristics of the deposited Ge layer for different annealing conditions.**

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>450 °C, 30 min</th>
<th>750 °C, 30 min</th>
<th>900 °C, 10 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-deposited</td>
<td>poly</td>
<td>poly</td>
<td>poly + single XTAL</td>
</tr>
<tr>
<td>(Fig. 1)</td>
<td>(Fig. 1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>as-deposited</td>
<td>poly + single XTAL</td>
<td>poly + single XTAL</td>
<td></td>
</tr>
<tr>
<td>(Figs. 1, 2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>as-deposited</td>
<td>single XTAL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Fig. 1)</td>
<td></td>
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**FIG. 5. Schematic illustration of the relation between the delay time for epitaxial growth due to the presence of an interfacial impurity layer and the nucleation time for the formation of polycrystals with the temperature.**
cally cleaned interface then doubtlessly contains impurities such as O, C and F that will produce a delay time before a detectable epitaxial growth starts. (b) The delay time $t_d$ changes with the annealing temperature more rapidly than the nucleation time $t_n$ does, as shown schematically in Fig. 5. The two lines for the delay time in Fig. 5 refer to two different interfacial impurity thicknesses. Since the interfacial thickness is not controlled and likely to be nonuniform, we may view the two lines for the delay time as those for the maximum and for the minimum thicknesses of the interfacial impurity in a sample. If the first annealing temperature is low, say at $T_a$, the delay time is everywhere longer than the nucleation time and we will observe a transition from amorphous to polycrystalline structure everywhere on the deposited layer. If the initial annealing temperature is $T_a$, the delay time is comparable with nucleation time and we anticipate the growth of epitaxial columns at spots where the interfacial oxide is thin, but where the oxide layer is thick, polycrystalline nucleation will start first. Finally, if the annealing temperature is at $T_a$, the nucleation time exceeds the time necessary for the epitaxial growth and the result will be the formation of an epitaxial layer without formation of polycrystallites.

With this model our experimental results can be explained in a straightforward fashion as shown in Fig. 6. An annealing temperature of 450 °C corresponds to a temperature such as $T_a$, where the nucleation of polycrystalline grains in the deposited layer occurs without epitaxial growth from the underlying crystal. As a result, a second annealing at 750 °C will not produce any realignment due to a lack of epitaxial columns. Further annealing at a temperature as high as 900 °C will produce the alignment of the crystallites with the single-crystal Ge substrate by a grain growth process as was demonstrated in the Si case. The annealing temperature of 900 °C ($T/T_m = 0.97$) is higher than the temperature used in the Si case, where $T/T_m = 0.8$ possibly due to a thicker oxide layer in the Ge case. An annealing temperature of 750 °C corresponds to $T_a$, where growth of epitaxial columns and nucleation of polycrystallites occur simultaneously. A good epitaxial layer can then be obtained only by the realignment of the polycrystallites with the adjacent epitaxial columns and the substrate after prolonged annealing. But the quality of the crystal so obtained is worse than the quality of the crystal that grows by annealing directly at 900 °C which corresponds to $T_a$. Now the growth is epitaxial everywhere without any polycrystalline formation.

In conclusion the epitaxial growth mechanism is different for the different time-temperature treatments. The structural morphology of the grown layer is not a simple function of the final time and annealing temperature. The relationship of the growth process to the temperature scale is a function of the cleanliness of the interface between the crystalline substrate and the deposited layer. Samples prepared using different cleaning procedures will show the same general behavior, but not necessarily at the same temperature. This conclusion is indeed a commonly observed feature in solid-phase epitaxy of deposited layers and is the reason why all results reported in this paper were measured on samples produced in a single evaporation.

ACKNOWLEDGMENTS

We would like to thank R. Fernandez and R. Gorris for their technical assistance, Dr. W. Mayer for clarifying discussions, and Dr. G. Foti for supplying the Ge wafers. The partial financial support by the Office of Naval Research is thankfully acknowledged (L. R. Cooper and G. B. Wright).