Crystallization of Ge and Si in metal films. II*

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Heat treatment of evaporated Si in contact with Ag films and Ge in contact with Al films results in the formation of precipitates of the semiconductor in a metal matrix. The structure of these precipitates was studied by transmission electron microscopy and diffraction (TEMD) and MeV ^{4}He ion channeling techniques. TEMD studies showed that the semiconductor precipitates were crystalline in nature. Channeling techniques showed that the crystallites did not have a simple orientation relationship with the underlying single-crystal substrate.

I. INTRODUCTION

Metal-semiconductor interactions play a major role in contact formation in semiconductor devices. To form low-resistance Ohmic contacts, it is standard practice to follow the evaporation of the metal layer with a heating cycle.[1] During this process pronounced reactions can take place between the semiconductor and the metal film. For example, in systems exhibiting a simple eutectic behavior, such as Si-Al,[2] Si-Ag,[3] and Si-Au,[4] Si can dissolve and migrate in the metal at temperatures well below the eutectic temperatures. Also, in systems where compound phases exist, formation of these compounds has been observed at low temperatures.[5,6]

Dissolution and diffusion phenomena have been utilized to demonstrate solid-phase epitaxial growth of both Si and Ge from Al layers. In these cases, the metal-semiconductor system is first heated isothermally to saturate the Al film with Si or Ge, and then it is cooled to achieve supersaturation; the excess Si or Ge regrows epitaxially on the underlying single-crystal substrate.[7,8] This process was carried out at temperatures below the eutectic point.

There have been studies of the crystallization of amorphous Si and Ge films in contact with metal layers. It has been found that crystallization occurs at lower temperatures than in the absence of the metal layer.[9,10] We have earlier used backscattering and scanning electron microscopy (SEM) to study the behavior of amorphous Si layers in contact with Ag films and Ge in contact with Al films.[11] In Paper I[12] we found that large precipitates of the semiconductor are formed in the metal layer when the system is heated at a constant temperature below the eutectic point. The purpose of this work is to study the nature of these precipitates. We have used transmission electron diffraction to determine if the precipitates are crystalline and MeV ^{4}He ion channeling effect measurements to find if the precipitates had any orientation relation to the underlying crystalline substrate.

II. EXPERIMENTAL

Sample preparation for backscattering measurements was described in detail in Paper I. The same preparation technique was used for channeling investigations. In brief, samples were prepared by evaporating either Si or Ge under conditions such that amorphous films were produced. The substrates were ⟨111⟩- or ⟨110⟩-oriented Si and Ge wafers and in a few cases vitreous carbon. In the same pumpdown, the semiconductors were overcoated with evaporated metal to form Ge/Al and Si/Ag composites. In some cases, the evaporation sequence was reversed. After evaporation, the samples were immediately heated and quenched in a dry N_2 atmosphere. The samples described here were heat treated for 1—13 h at temperatures of 300 °C for Ge/Al and 700 °C for Si/Ag.

Transmission electron microscopy and diffraction (TEMD) at 100 kV were employed to study the structure of the initial and heat-treated Ge/Al and Si/Ag films. To study the as-deposited composite structures, samples were prepared in the following fashion. First, a thin (~30-Å) carbon film was deposited on a microscope grid.[13] Next, the metal layer was deposited on the carbon-coated grids, and this was followed by the deposition of the semiconductor layer. Samples prepared in

FIG. 1. Bright-field image of 1000-Å Al and 500-Å Ge composite film deposited on a carbon substrate. The inset in the upper right-hand corner is the corresponding selected-area diffraction pattern.

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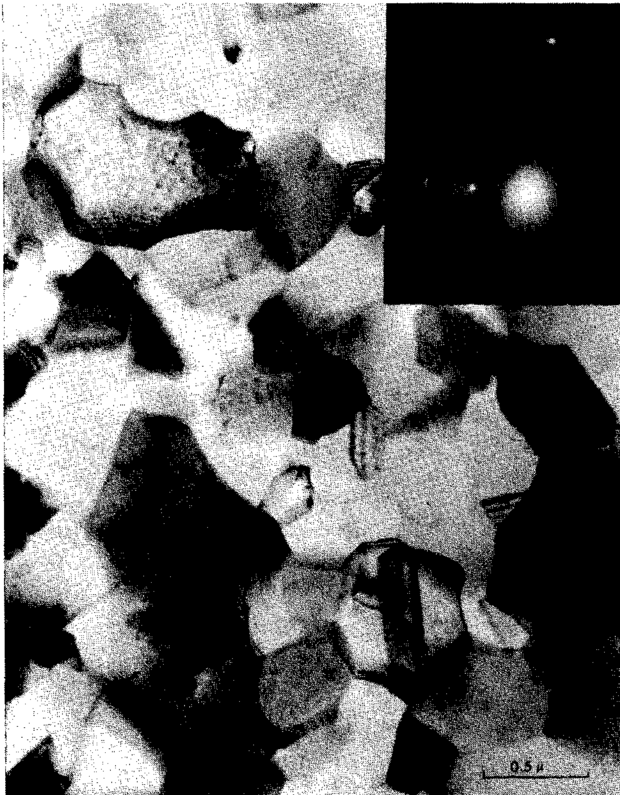

FIG. 2. Bright-field image of a 3400-Å Al and 1940-Å Ge composite film deposited on a silicon substrate and heated for 10 h at 300 °C. The inset in the upper right-hand corner is the selected-area diffraction pattern from a 2250-Å Al and 115-Å Ge composite after heat treatment at 300 °C for 13 h.

this way were only used to characterize the initial condition of the films.

The same samples as were used for backscattering measurements (Paper I[12]) were also used to investigate the structure of the precipitates. This was accomplished by stripping with cellophane tape the composite films from the substrate (carbon substrates for the Si/Ag case and Si substrates for the Ge/Al case). The thin films were removed from the tape by soaking in chloroform. They were then picked from the chloroform on 400-μm electron microscope grids, and the specimens were dried prior to TEMD study.

III. RESULTS AND DISCUSSION

A. Transmission electron microscopy and diffraction

Structurally, the initial specimens were quite similar; both Ge/Al and Si/Ag specimens consisted of a polycrystalline metal layer and an amorphous semiconductor layer. A typical morphology is shown in Fig. 1, which is a bright-field image of a Ge/Al structure. The average grain size of the Ge/Al specimens was found to be approximately 0.1 μm, and for the Si/Ag specimens the grain size varied between 0.01 and 0.1 μm. The associated selected-area diffraction pattern of Fig. 1 is shown as an inset. The diffraction pattern clearly shows a superposition of two diffraction patterns: one polycrystalline pattern and one amorphous pattern (all diffraction patterns in this work were analyzed by using a polycrystalline Au specimen as a diffraction standard). An analysis of Fig. 1 showed the polycrystalline diffraction pattern to be from the Al layer and the amorphous pattern to be from the Ge layer. It should be pointed out that the diffraction contribution from the amorphous carbon layer to Fig. 1 was negligible owing to the extreme thinness (~30 Å) of the carbon support film. Finally, there was no apparent preferred orientation of the metal layer in any of the initial samples.

As is described in Sec. II, some of the specimens used for heat treatments were deposited on single-crystal Si or Ge. The initial structure of these samples may differ slightly from those made on carbon-covered microscope grids or vitreous carbon. However, the main structural feature of the initial samples—i.e., a polycrystalline metal layer and an amorphous semiconductor layer—should be the same in all samples.[14,15]

After thermal treatment, both the Ge/Al and the Si/Ag specimens were polycrystalline with no identifiable amounts of amorphous material. Samples from both systems consisted of a mixture of pure semiconductor crystallites interdispersed in a matrix of metal crystallites. Figure 2 shows the bright-field image and selected-area diffraction pattern of a Ge/Al sample that had been heated for 10 h at 300 °C. The average grain size was 0.3 μm. The diffraction pattern of a Ge/Al sample heat treated at 300 °C for 13 h is shown as an

FIG. 3. Bright-field image of a 1700-Å Ag and 400-Å Si composite film deposited on a carbon substrate and heated for 2 h at 700 °C. The inset is the selected-area diffraction pattern, which indexes for Si oriented approximately ⟨110⟩.

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inset in Fig. 2. This diffraction pattern shows that no detectable amounts of amorphous material were present after heat treatment.

Figure 3 shows a bright-field image of a Si/Ag sample treated for 2 h at 700 °C, and the inset shows the corresponding selected-area diffraction pattern. The diffraction pattern again indicates the absence of amorphous material. The selected-area diffraction pattern shows Si oriented approximately ⟨110⟩. The extra reflections are due to double diffraction and twinning.

Stereographic and contrast analysis of the heat-treated specimens did reveal one difference between the morphology of the Ge/Al specimens and the Si/Ag specimens: In the Ge/Al specimens the semiconductor crystals were pyramidal in nature, whereas in the Si/Ag specimens the semiconductor crystallites were more prismlike.

B. Channeling effect measurements

In channeling measurements the incident ion beam (2-MeV $^4He^+$ was used in this work) is aligned parallel with a low-index crystallographic axis of the single-crystal substrate.[16,17] The number of backscattered particles shows a large reduction in this aligned geometry compared with the case where the beam is not aligned with a major crystal axis (hereafter called random incidence). For the Si and Ge single-crystal samples used in this study there is typically a factor-of-30 reduction of the backscattering yield on uncovered portions of the samples.

Channeling measurements are sensitive to the condition of the crystal; i.e., crystal imperfection will increase the ratio of aligned to nonaligned scattering yield.[17] For example, the channeling technique has been used to study properties of heteroepitaxial layers of Si on spinel.[18] Depth distributions of the concentration of crystal imperfections in the Si layer were found from analysis of channeling spectra. On solid-phase-grown Ge layers, channeling measurements were used to show that the regrown layer was epitaxial with the underlying single-crystal Ge.[8]

Figure 4 shows random and aligned spectra for a sample with 220 Å of Ge and 4000 Å of Al heated at 300 °C (see Paper I[12] for details of backscattering equipment). As was discussed in Paper I, the composition of the film is reflected directly in the random spectrum. The backscattering yield from the Ge precipitates appears between 1.4 and 1.6 MeV. The contribution from the Ge substrate is found as a continuum below 1.4 MeV with the Al contribution superimposed.

The aligned spectrum was obtained by orienting the crystal with respect to the beam, while the ^4He ions were incident on a portion of the sample not covered by Al. The beam was then translated onto an Al-covered portion. As is shown in Fig. 4, the ratio of random to aligned yield was about 3 for the Ge substrate. The increase in the aligned yield in the substrate is not due to disorder but is caused by multiple scattering of the ^4He ions in the Al film.[19] In Fig. 4 there is no reduction in the aligned yield for the portion of the spectrum corresponding to the Ge crystallites. This indicates

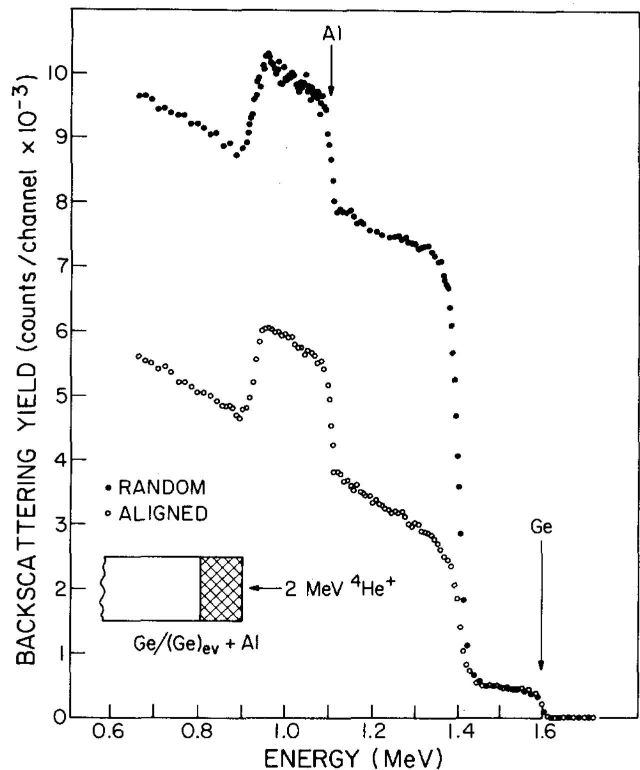

FIG. 4. Random and aligned energy spectra for 2-MeV ^4He ion scattering from a Ge/Al sample heat treated at 300 °C. The sample was prepared by depositing 220 Å of Ge, which was followed by the deposition of 4000 Å of Al, onto a Ge ⟨110⟩ single crystal. The arrows indicate the energy position for a scattering from atoms at the surface.

that the crystallites are not epitaxial with the underlying single-crystal substrate. If the crystallites were predominately oriented with the substrate, the aligned yield would exhibit a pronounced reduction, compared with the random yield. Multiple scattering effects should not influence the aligned yield because the Ge crystallites extend throughout the film.

A somewhat different approach was used to investigate channeling effects in the Si/Ag system. In this case the Ag was etched away, which left islands of precipitates on the Si substrate. This eliminates the increase in substrate aligned yield caused by multiple scattering in the Ag layer.

Figure 5 shows random spectra (before etching) for samples with 2000 Å of Ag covered by 1350 Å of Si for both the as-evaporated case and the case after heat treatment at 700 °C for 5 and 60 min. The spectrum for the as-deposited condition is shown in the top portion of Fig. 5. The energy corresponding to scattering from atoms at the surface is represented by arrows in the figure. The high-energy edge of that portion of the spectrum corresponding to Ag is shifted to lower energies because of the energy loss of the ^4He particles in inward and outward trajectories in the overlying Si layer. Upon heat treatment (the lower spectra in Fig. 5), the Ag portion broadens and shifts to the surface position. The Si portion spreads to lower energies with a very low yield at its original position. After 700 °C annealing for 60 min the shape of the spectrum shows

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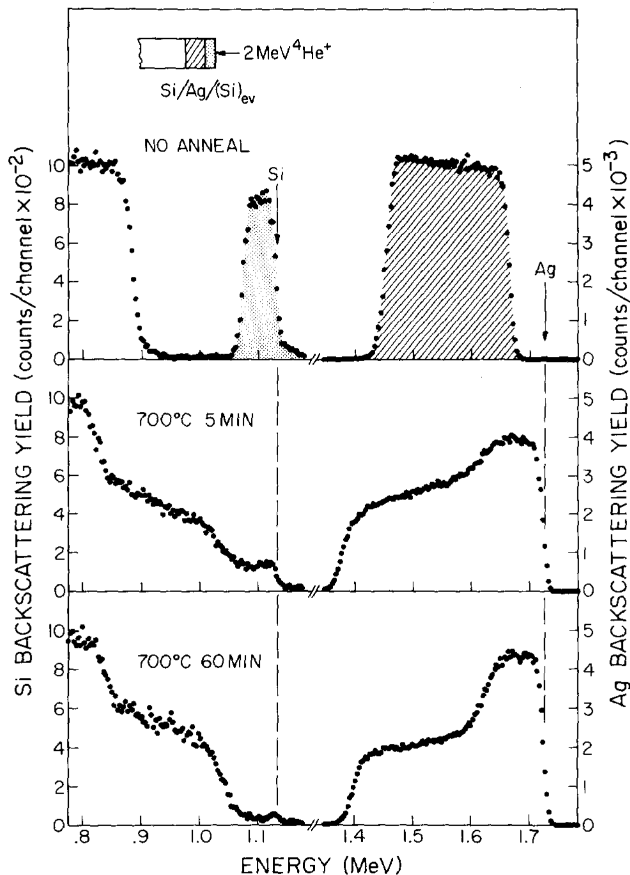

FIG. 5. Random energy spectra for 2-MeV ^{4}He ion scattering from Si/Ag samples. The top portion of the figure shows the as-deposited spectrum for 2000-Å Ag overcoated with 1350-Å Si on a Si ⟨110⟩ single-crystal substrate. The middle and lower portions show spectra after heat treatments at 700 °C for 5 and 60 min, respectively. The arrows again indicate the energy position for scattering from atoms at the surface.

that the evaporated Si has formed islands in contact with the underlying substrate. These islands extend through approximately two-thirds of the composite film structure. The Ag fills in the space between the Si islands as well as forms a layer, of approximately one-third of the composite thickness, at the surface. This interpretation was verified by scanning electron micrographs on samples where the Ag has been selectively removed by etching in dilute ferric nitrate.

Channeling measurements were performed on the same sample used for the lower spectrum in Fig. 5; however, for the channeling measurements the Ag was removed. The corresponding aligned and random spectra are presented in Fig. 6. If the Si crystallites were epitaxial, they would show the same channeling properties as do the Si substrate—i.e., a 30-fold reduction of the aligned yield compared with the random yield. This case is indicated in Fig. 6 by a dashed line. From scanning electron micrographs it was found that the Si islands occupied approximately 60% of the surface area. This information can also be obtained from the backscattering spectrum in Fig. 5 by comparing the heights of signals from Si in the substrate and from Si in the precipitates. If the crystallites did not have any preferred orientation, the corresponding scattering yield would be 60% of the random yield. This case is represented by the dot-dashed line in Fig. 6. The measured aligned energy spectrum falls between these two extreme cases. The same ratio of aligned to random yield for scattering from the Si crystallites was obtained when the beam energy was changed to 1 MeV. The critical angle for channeling in ⟨110⟩ Si is 0.53° for 2-MeV ^{4}He and 0.75° for 1-MeV ^{4}He. The fact that there was no change in the aligned-to-random ratio in going from 2 to 1 MeV indicates there were no crystallites aligned within 0.53° and 0.75°. The fact that the aligned-to-random ratio at 2-MeV beam energy is roughly half that expected for random crystallite orientation suggests that approximately half of the Si crystallites are epitaxial with the underlying Si substrate (see Appendix).

The high-energy portion of the spectra in Fig. 6 shows a distribution between 1.6 and 1.7 MeV, corresponding to scattering from Ag. The amount of residual Ag remaining after the ferric nitrate etch can be obtained by comparing the Ag yield with the Si random yield. This Ag is probably not incorporated within the Si crystallites as solid solubility of Ag in Si is very low.[20] If it was, however, uniformly distributed within the Si, it would correspond to approximately 0.1 at.%. The peak at 1.5 MeV is due to scattering from Fe contamination remaining after the Ag was removed by ferric nitrate etch.

IV. SUMMARY

We have studied the nature of semiconductor precipitates formed during heat treatment of evaporated layers of Si in contact with Ag films and Ge in contact with Al films.

TEMD analysis revealed that the initial structure of the samples consisted of an amorphous semiconductor layer and a polycrystalline metal layer. After heat treatment the structure of both the Si/Ag and Ge/Al samples was found to be polycrystalline: semiconductor crystal-

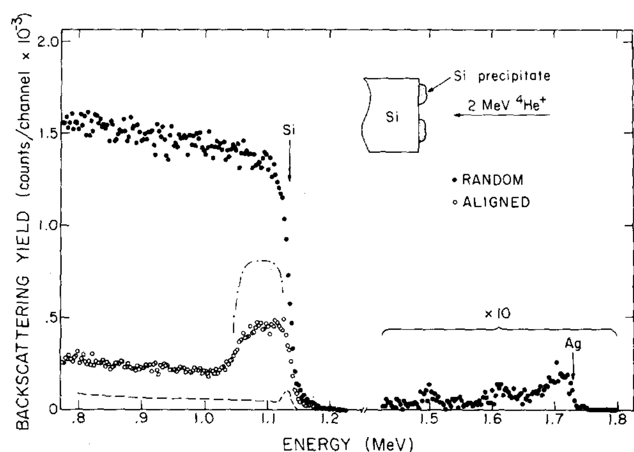

FIG. 6. Random and aligned energy spectra for 2-MeV ^{4}He ion scattering from a Si/Ag sample heat treated at 700 °C for 60 min (same sample as is shown in the lower portion of Fig. 5). In this case the Ag matrix has been selectively removed. The dashed line indicates the aligned yield from a single-crystal substrate. The dot-dashed line indicates the expected aligned yield if the Si precipitates were randomly oriented.

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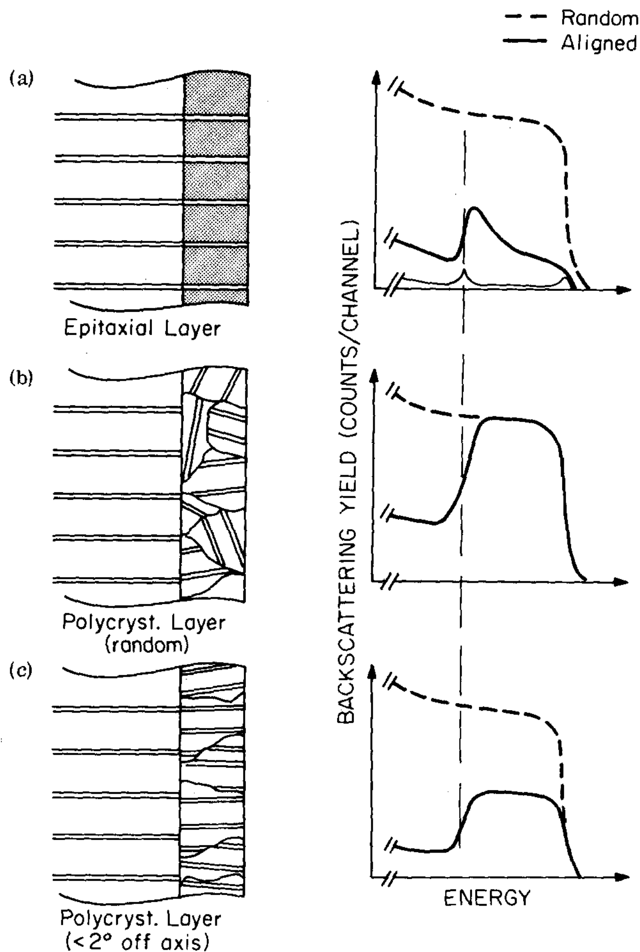

FIG. 7. Sketches of the structures and schematic random and aligned energy spectra for MeV ^{4}He ion scattering from epitaxial layers on single-crystal substrates. The double lines in the left-hand sketches indicate the orientation of a major crystallograhic axis. (a) The spectrum show an epitaxial layer (light line) and an epitaxial layer containing a high number of lattice imperfections (thick line). The imperfections are indicated on the left-hand sketch by shading. The spectra in (b) represent the case of a randomly oriented polycrystalline layer, and (c) shows the case of a textured polycrystalline layer with a strong preferred orientation. The vertical dashed line indicates the position of the interface.

lites intermixed in a matrix of metal crystallites. There were no identifiable amounts of amorphous material present in the thermally treated samples. We conclude that the amorphous semiconductor had dissolved in the metal film and was transformed into a crystalline state.

MeV ^{4}He ion channeling measurements showed that the semiconductor crystallites were mostly not oriented with respect to the underlying single-crystal substrate.

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APPENDIX

Channeling effect measurements can give information on the crystalline nature of a layer on a single-crystal substrate. One can obtain information on the amount of preferred orientation[21] and, in the case of epitaxial layers, the depth distribution of lattice imperfections.[18]

There are limitations to the applicability of the channeling technique to the evaluation of ordered layers on single-crystal substrates. The schematic diagrams in Fig. 7 illustrate some of these limitations. Three cases are shown: (a) an epitaxial layer of Si grown on a Si substrate; (b) a polycrystalline Si film with no preferred orientation, and (c) a polycrystalline film with a strong orientation of the crystallites. In these channeling spectra the beam is aligned with a major axis of the underlying crystal substrate.

The epitaxial layer case (a) has been investigated by several groups.[8,18,21] The perfectly epitaxial case [light line in Fig. 7(a)] cannot be separated from a single crystal except for a small peak usually appearing at the energy position of the interface between the epitaxial layer and the substrate. If the layer contains a high number of lattice imperfections, the aligned yield is increased as indicated in Fig. 7(a) by the thickly drawn curve. To extract the density of lattice defects from channeling spectra, it is necessary to separate the contribution due to direct backscattering from lattice imperfections and dechanneling caused by forward scattering from the crystal imperfections.[18] Note that channeling is not sensitive to the low concentration of defects that are of interest to evaluate the electrical properties of epitaxial semiconductor layers. For single alignment cases concentrations of scattering centers of 1% can be detected, and with double alignment approximately 0.1% can be detected.[17]

The case of highly polycrystalline or amorphous layers on Si substrates is much more straightforward to handle. Since there are no preferred orientation directions in the film, no channeling behavior is observed. Such cases have, for example, been studied in ion implantation investigations.[17] The amount of dechanneling (as evidenced by the height of the aligned yield from the crystal substrate) can be directly calculated from knowledge of the amount of multiple scattering in the film and from the measured critical angle for channeling of the substrate.[19]

The case of a polycrystalline film where the crystallites are highly oriented with respect to the substrate can also be described rather simply. Those crystallites which are oriented with crystal axes within approximately $\frac{1}{5}$ of the critical angle will have the same channeling behavior as the underlying crystal substrate. For MeV ^{4}He ions, the critical angle for channeling is of the order of 1°. Crystallites with their axes oriented between approximately $\frac{1}{5}$ and 1 times the critical angle exhibit strong dechanneling behavior. Crystallites lying outside the critical angle will exhibit random yield. Figure 1(c) describes the situation where approximately $\frac{1}{2}$ of the crystallites are closely aligned with the underlying substrate. One can obtain information on the distribution of crystalline orientation by changing the beam energy or beam species, which leads to changes in the critical angle: $\psi_{1/2} \propto Z_1/E^{1/2}$.[21]

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