Heterostructure by solid-phase epitaxy in the Si⟨111⟩/Pd/Si(amorphous) system

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When a thin film of Pd reacts with a ⟨111⟩ Si substrate, a layer of epitaxial Pd_2Si is formed. It is shown that Si can grow epitaxially on such a layer by solid-phase reaction.

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INTRODUCTION

It has been demonstrated recently that electrically active epitaxial layers of Si can be grown from an amorphous source by solid-phase reaction through a Pd-silicide layer.[1-3] The sample configuration consists of a Si single-crystal substrate onto which a layer of Pd (~1000 Å) and a layer of amorphous Si (~1 μm) are deposited. The processing steps are to first anneal the sample at ~300 °C to induce the formation of Pd_2Si and then to anneal the sample at higher temperatures (~500 °C) to promote epitaxial growth of Si from the amorphous source onto the single-crystal substrate. Only ⟨100⟩ Si substrates were used so far in investigations of this solid-phase epitaxial growth (SPEG). This substrate orientation leads to homoepitaxy, i.e., epitaxial growth of Si on the Si substrate, as just described. The process is demonstrated in the MeV ^4He backscattering spectra[4] shown in Fig. 1(a). The solid line in Fig. 1(a) depicts the energy spectrum for a virgin sample and the dots represent the energy spectrum for the same sample annealed to the final stage. After heating, the Pd signal decreases in amplitude due to silicide formation and moves to higher energies, indicating that amorphous Si has been displaced from the sample surface by Pd-silicide and has grown onto the ⟨100⟩ substrate (shaded area). The epitaxial nature of the grown layer has been established by glancing x-ray diffraction and by channeling techniques.[1]

Here, we report that by taking advantage of the epitaxial characteristics of the Pd_2Si formed on ⟨111⟩ Si substrates, using the initial sample configuration of (⟨111⟩Si)/Pd/(amorphous Si), the solid-state reaction can lead to heteroepitaxy, i.e., SPEG of Si layers on the single-crystal Pd_2Si layer.

EXPERIMENTAL

In this investigation, ⟨111⟩-oriented Si samples (1–10 Ω cm, *n* type) were used. The commercial wafers with a chemomechanical polished surface were first cleaned with organic solvents, rinsed with water, and then immersed in a diluted HF solution. This solution was then quenched with water and the samples were immediately loaded into the evaporation chamber equipped with an ion pump. A thin layer of Pd (~2000 Å) was first deposited onto the wafers by electron-gun evaporation at a rate of about 5 Å/sec, followed by the deposition of Si (~3000 Å) at a rate of about 100 Å/sec. The pressure during evaporation was kept below 1×10^{-6} Torr.

The samples were annealed in a quartz-tube furnace at a pressure of 2.5×10^{-6} Torr. The process cycle was to first heat the sample at 400 °C for 30 min to form Pd_2Si and then, without breaking the vacuum, to increase the temperature to about 500 °C.

The formation of Pd_2Si and the growth kinetics were studied by MeV $^4He^+$ backscattering spectrometry.[4]

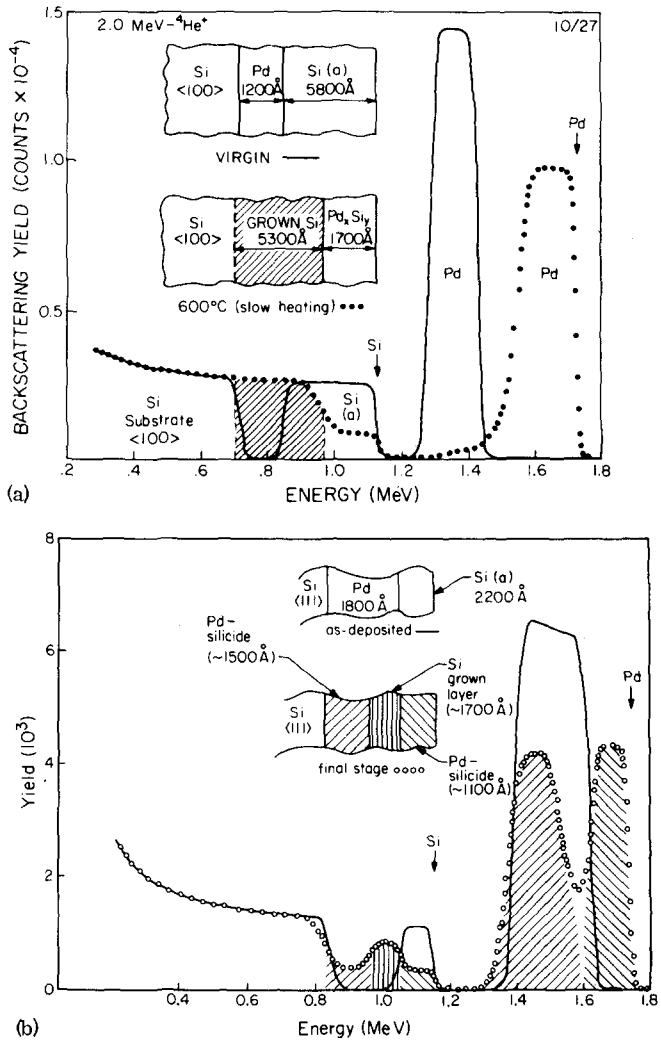

FIG. 1. (a) Backscattering energy spectra for a ⟨100⟩ sample in the as-deposited condition and after anneal to the final stage. The arrows indicate the surface positions for the two elements. The Pd is seen to have moved to the surface of sample after annealing. The shaded area represents the layer of Si added to the substrate by SPEG. (b) Backscattering spectra for a ⟨111⟩ sample in the as-deposited condition and after anneal to the final stage. The Pd signal is split into two locations, indicating a heterostructure.

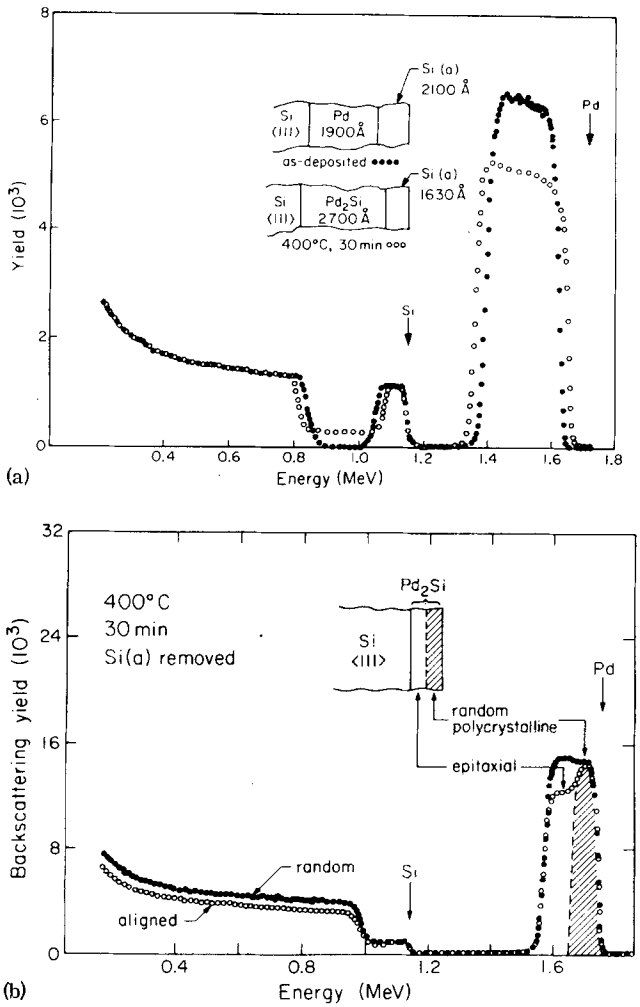

FIG. 2. (a) Backscattering energy spectra for a ⟨111⟩ sample in the as-deposited condition and after anneal to form Pd_2Si. The spread of the Pd signal to both lower and higher energies shows that both the ⟨111⟩ Si substrate and the amorphous layer were partially consumed in the silicide formation. (b) Aligned and random spectra for a similar sample shown in (a), but with thinner Pd and with the top amorphous Si layer removed after silicide formation. The aligned spectrum shows that about half of the Pd_2Si layer near the sample surface is polycrystalline in nature and the other half near the substrate is epitaxial in nature.

The epitaxial nature of the grown layers was studied by glancing x-ray diffraction and by channeling measurements.[1,4]

RESULTS AND DISCUSSION

Investigations on the formation of Pd-silicide in thin-film systems showed that thin Pd layers react with single-crystal or amorphous Si substrates to form a Pd_2Si phase in the temperature range of about 100–700 °C.[5–11] The growth rates of Pd_2Si on ⟨100⟩, ⟨110⟩, and ⟨111⟩ single-crystal Si substrates and on amorphous Si layers are essentially the same.[5] Furthermore, Pd_2Si layers form epitaxially on ⟨111⟩ substrates, but assume a rather random polycrystalline structure on amorphous Si substrates. Figure 2(a) shows the backscattering spectra of a sample with a configuration of (⟨111⟩ Si)/Pd/(amorphous Si) in the as-deposited condition, and after annealing at 400 °C for 30 min to form Pd_2Si. After annealing, the Pd signal decreases in amplitude and increases in width. The ratio of height of the Pd signal (at about 1.5 MeV) to the height of Si (at about 0.9 MeV) indicates the formation of Pd_2Si. The Pd signal widens towards both low and high energies, which shows that about equal portions of crystalline (⟨111⟩ Si) and amorphous Si are consumed in the silicide formation. Figure 2(b) shows that half of the Pd_2Si layer which formed with the ⟨111⟩ Si substrate is single crystalline in nature and epitaxial with respect to the ⟨111⟩ Si substrate, and that the other half of the Pd_2Si layer which formed with the amorphous Si layer is polycrystalline. Figure 2(b) shows an energy spectrum of backscattered He particles incident in a random and a ⟨111⟩-aligned direction with respect to the substrate for a sample similar to that shown in Fig. 2(a), but with thinner layer of Pd_2Si. The top amorphous Si was removed by chemical etching after the silicide formation to reduce dechanneling. The lower backscattering yield centered at about 1.6 MeV for the Pd signal in the aligned case indicates that approximately 50% of the Pd_2Si layer (formed by reacting Pd with ⟨111⟩ Si) has single-crystal characteristics. This layer with ⟨111⟩-aligned backscattered yield of about 75% of the random yield has a mosaic structure and contains small-angle boundaries with misorientation of about 1°.[5] The other 50% of the Pd_2Si layer which formed with amorphous Si is composed of random polycrystallites; the Pd signal, therefore, does not change for an aligned incident beam.

When a sample with such a structure is annealed further to induce solid-phase epitaxial growth with the remaining amorphous Si, one observes that it is the epitaxial Pd_2Si layer which acts as the growth substrate. As a result, an epitaxial Si layer is grown on a single-crystal Pd_2Si layer, thus forming a heterostructure. Figure 1(b) shows backscattering spectra for a sample in the as-deposited condition, and annealed to the final stage. The Pd signal at ~1.7 MeV for the annealed sample is generated by the Pd in the polycrystalline silicide layer which has been displaced to the sample surface after the epitaxial growth of Si. The Pd signal at ~1.5 MeV is due to the Pd in the epitaxial silicide layer. The Si signal at ~1 MeV represents the Si layer grown onto the epitaxial Pd-silicide layer. The yield of this Si signal is somewhat lower than expected for pure Si. This could be due to a lateral nonuniformity of the interface between the top polycrystalline Pd-silicide layer and the epitaxial Si below and/or a lateral nonuniformity between the epitaxial Si and the epitaxial Pd-silicate layer. The comparison of the spectra shown in Figs. 1(a) and 1(b) clearly reveal the difference of SPEG on ⟨100⟩ Si [Fig. 1(a)] and ⟨111⟩ Si substrates.

The epitaxial nature of the grown Si layer in the ⟨111⟩ case was ascertained by glancing x-ray diffraction patterns and by channeling measurements after the top polycrystalline Pd-silicide was removed by chemical etching. X-ray results indicate that the grown Si layer and the underlying Pd-silicide layer are both single-crystal in nature, as shown in Fig. 3. Channeling measurements are in agreement with x-ray diffraction results. The crystal quality of the Si layers grown on

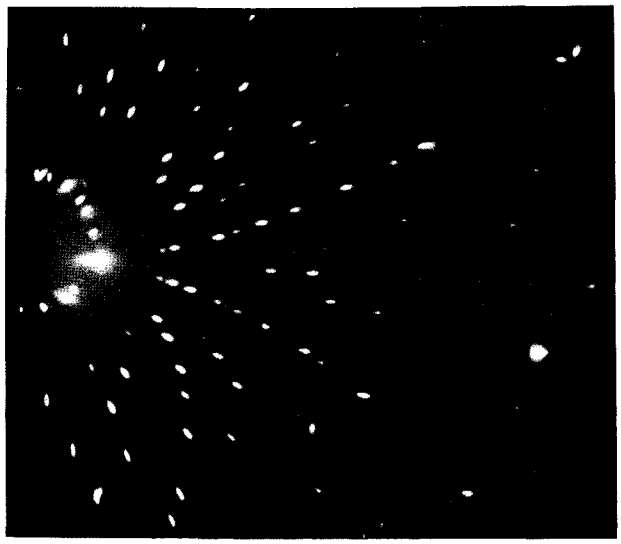

FIG. 3. Glancing x-ray diffraction pattern (Read camera) of the sample shown in Fig. 1(a) after the removal of the top polycrystalline Pd-silicide layer by chemical etching. The dot pattern indicates the single-crystal nature of the Si grown layer and the underlying Pd-silicide layer.

the epitaxial Pd-silicide is not as good as that of layers grown on ⟨100⟩ Si substrates. This is evidenced by the relatively high ratio of channeled yield to random yield in the backscattering spectra of the former. The reason is probably related to the fact that the epitaxial Pd-silicide layer onto which the Si grows has similar backscattering characteristics. In that case, the cause is the mosaic structure of the epitaxial Pd_2Si.[12]

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