Growth mechanism for solid-phase epitaxy of Si in the Si ⟨100⟩/Pd_2Si/Si(amorphous) system studied by a radioactive tracer technique*

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A tracer technique using radioactive ^{31}Si ($T_{1/2} = 2.62$ h) was used to study solid-phase epitaxial growth (SPEG) of silicon. After depositing Pd and Si onto single-crystal substrates which had been activated in a nuclear reactor, Pd_2Si was formed with about equal amounts of radioactive and nonradioactive silicon during heating at 400°C for 5 min. After a second annealing stage (450°C→500°C in 1 h) the silicide layer which moves to the top of the sample during SPEG was etched off with aqua regia. From the absence of radioactive ^{31}Si in the etchant solution it is concluded that SPEG takes place by dissociation of the Pd_2Si layer at the single-crystal interface to provide free Si for epitaxial growth, while new silicide is formed at the interface with the amorphous Si. These results were confirmed by evaporating radioactive silicon onto nonactivated silicon substrates before evaporation of Pd and stable amorphous Si and by measuring the activity in the SPEG sample before and after etching off the silicide layer.

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INTRODUCTION

Electrically active epitaxial layers of Ge and Si have recently been grown on single-crystal substrates by means of solid state reactions.[1–5] Samples used for this purpose usually have a composite structure of single-crystal substrate/metal/amorphous semiconductor, such as the Ge(xtal)/Al/Ge(amorphous) system. Upon heating at a suitable temperature the amorphous material grows epitaxially on the single-crystal substrate and the driving force for solid-phase epitaxial growth (SPEG) in these systems is believed to be the higher free energy of the amorphous state as compared to that of the crystalline form. In the case of the Ge(xtal)/Al/Ge(a) system, the Al layer acts as a dissolution and transport medium through which the amorphous Ge atoms can diffuse. For the Si(xtal)/Al/Si(a) systems, however, it was found that a thin native oxide layer on the single-crystal substrate often prevents the uniform growth of epitaxial layers.[2] However, this problem was solved by selecting Pd as the metal layer[3] because during an initial heating stage at approximately 300 °C the Pd reacts with both single-crystal and amorphous silicon to form Pd_2Si, thereby ensuring very clean interfaces essentially free of oxygen. When such samples are heated at still higher temperatures (approx. 500 °C), nice uniform epitaxial layers of Si can be grown.

There is much interest in the role that the silicide layer plays during SPEG in the Si(xtal)/Pd_2Si/Si(a) system. Two possible mechanisms can be postulated. Amorphous Si can diffuse through the Pd_2Si layer by interstitial and/or grain-boundary diffusion to the single-crystal-crystal interface. In this case the silicide layer only acts as a medium for the Si transport, similar to the Si(xtal)/Al/Si(a) system.[2] On the other hand, the Pd_2Si layer can dissociate to provide free Si for epitaxial growth at the palladium-silicide—single-crystal interface, while new silicide is formed at the interface with the amorphous silicon ("dissociation" model). If there is no dissociation of the Pd_2Si, then in principle all silicide-forming elements could be possible candidates as a transport medium, provided the silicide formation temperature is below the recrystallization temperature of amorphous silicon in contact with a silicide. If the process takes place by a dissociation mechanism, the bond energy of the silicide is expected to be an important factor for successful epitaxial growth.

In this investigation the transport mechanism of silicon during solid-phase epitaxial growth in the Si(xtal)/Pd_2Si/Si(a) system has been studied using radioactive silicon as a tracer. The approach used can briefly be described as follows. Radioactive ^{31}Si is formed by irradiating single-crystal silicon wafers in a nuclear reactor. After depositing Pd and (nonradioactive) Si onto activated single-crystal substrates, Pd_2Si was formed with about equal amounts of radioactive and nonradioactive Si during heating at approximately 400 °C (see Fig. 1). After a second annealing stage (about 500 °C) this silicide layer, which moves to the top of the sample during

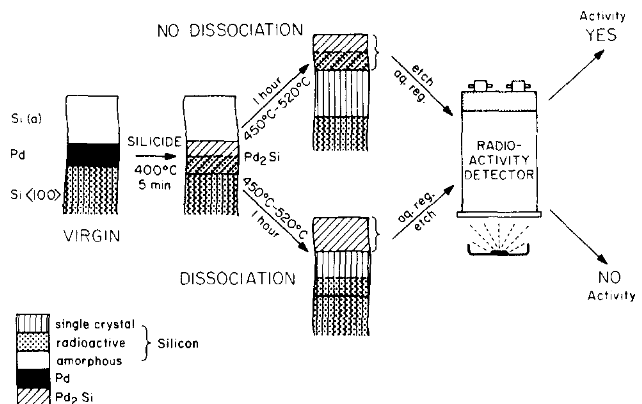

FIG. 1. Schematic diagram showing how radioactive ^{31}Si ($T_{1/2}$= 2.62 h) can be used to determine whether solid-phase epitaxial growth (SPEG) of Si takes place by a "dissociation" mechanism. The presence (or absence) of radioactivity in the top silicide layer after SPEG is determined by β counting after etching the silicide off with aqua regia.

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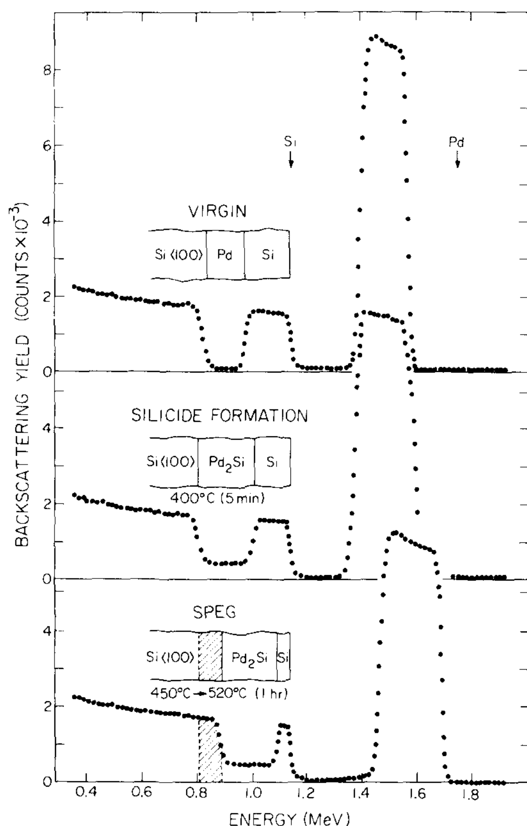

FIG. 2. Backscattering spectra measured with 2-MeV α particles of a sample in the as-deposited condition (virgin), after silicide formation and after SPEG. The epitaxially regrown silicide is shown by the crosshatched area in the bottom spectrum. This spectrum was measured at the end of the first transient stage of epitaxial growth.

SPEG, is etched off with aqua regia. From Fig. 1 it can be seen that by measuring the radioactivity in the Pd_2Si etch one can determine whether SPEG has taken place by a dissociation mechanism or not.

EXPERIMENTAL

Single-crystal silicon wafers (about 1 cm^2 in size) with polished surfaces and ⟨100⟩ orientation were first cleaned and then activated in a Triga nuclear reactor at the University of California, Irvine. During neutron activation radioactive ^{31}Si is formed from ^{30}Si (3.1 at.%) by the reaction $^{30}Si\ (n,\gamma)^{31}Si$ which has a cross section of 0.10 barns. Silicon-31 decays with a half-life of 2.62 h by emitting β particles (max. β^- energy = 1.48 MeV) for 99.93% of its distintegrations.

After activation, samples were first cleaned with organic solvents, etched in HF, rinsed in high-purity water, blown dry, and immediately placed into a vacuum deposition system. Palladium with thicknesses varying between 1000 and 2500 Å was then deposited onto the activated single-crystal substrates by electron-gun evaporation in a vacuum of approximately 5×10^{-7} Torr at a rate of 5 Å/sec. Immediately following the Pd evaporation, a layer of nonactivated amorphous Si (between 3500 and 6500 Å) was deposited by electron-gun evaporation from a carbon crucible, at a rate of approximately 100 Å/sec.

Annealing was performed in a vacuum quartz-tube furnace at typical pressures of 1×10^{-6} Torr. Samples were first annealed at 400 °C for 5 min for silicide formation. Rutherford scattering with 2-MeV α particles showed that the Pd usually reacted with equal amounts of radioactive single-crystal silicon and unactivated amorphous silicon, thereby ensuring very clean interfaces between layers. After silicide formation a higher-temperature vacuum annealing was carried out by heating from 450 to 520 °C over a period of 1 h for epitaxial growth of silicon.

After SPEG the silicide layer was etched off with aqua regia and the presence of β radioactivity from ^{31}Si was determined by measurement with an end-window Geiger-Müller counter having a mica window (1.8 mg/cm^2) with a cross-sectional area of 6 cm^2. Drying of the etchant solution had to be carried out before activity measurement to minimize β absorption losses. For an "in-core" thermal neutron flux of $7\times10^{12}\ n\,cm^{-2}\,sec^{-1}$ and a sample-to-detector distance of 1.3 cm, a zero count rate (normalized to a time corresponding to the end of the neutron activation) of approximately 20 000 cpm was obtained from 1000 Å of silicon per cm^2, after a 1-h irradiation.

To monitor the epitaxial growth and etching processes quantitatively, 2-MeV ^4He backscattering spectrometry was used.[6]

RESULTS AND DISCUSSION

Backscattering spectra of the same sample in the as-deposited condition (virgin), after silicide formation and after SPEG, are shown in Fig. 2. The Si and Pd arrows in Fig. 2 shows the energies corresponding to scattering from surface atoms of Si and Pd. After silicide formation the Pd signal decreases in amplitude and increases in width indicating the formation of a Pd_2Si layer between the single-crystal Si ⟨100⟩ substrate and the amorphous Si. From the positions of the single-crystal silicon edge and the lower-energy edge of the amorphous silicon it can be deduced that both the crystal substrate and amorphous Si layer are partially consumed in about equal amounts during silicide formation. When the Si ⟨100⟩/Pd_2Si/Si(a) structure is heated from 450 to 520 °C over a period of 1 h, SPEG takes place (see crosshatched area in bottom spectrum of Fig. 2). During solid-phase epitaxial growth of silicon the consumption of amorphous Si can be seen from the decrease in the width of the signal from amorphous Si. At the same time the silicide moves towards the top of the sample as can be deduced from the shift of the Pd signal to higher energies.

It has been found that the epitaxial silicon layer grows by island formation.[5] During a first stage, islands of Si form and grow laterally until they coalesce to form a uniform layer of epitaxial Si about equal in thickness to the original silicide layer. If there is still some amorphous silicon left at the end of the first stage, SPEG continues by a second stage of island formation but at a slower rate than the first stage.[7] This process continues periodically until all the amorphous Si is consumed. The spectrum at the bottom of Fig. 2 was measured at the end of the first stage.

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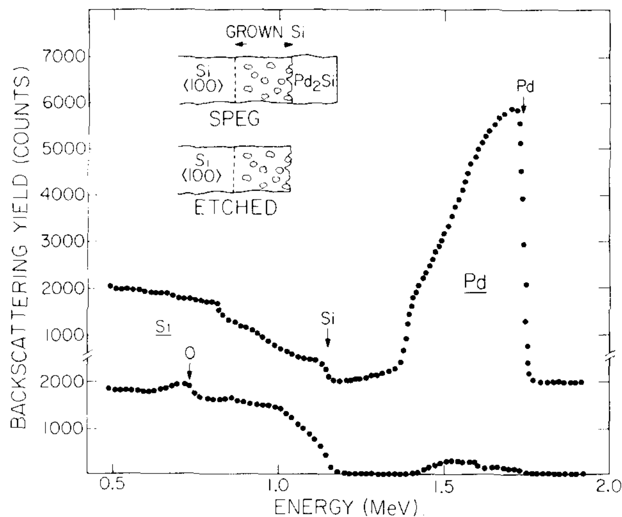

FIG. 3. Backscattering spectra of a SPEG sample before and after etching with aqua regia. The presence of a small amount of Pd in the etched sample is due to trapping of palladium silicide in the regrown silicon.

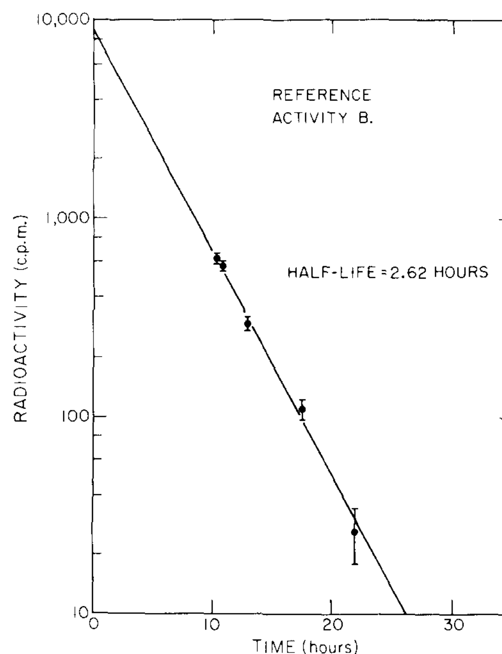

FIG. 4. The ^{31}Si activity measured in the etchant of reference sample B, as a function of time after the end of the neutron irradiation.

If SPEG is carried out until all the amorphous silicon is consumed, the silicide layer will move to the top of the sample and half of it will still be marked with radioactive Si atoms (see Fig. 1) if the process takes place without dissociation of the silicide. However, if silicon epitaxy proceeds by a "dissociation" mechanism, all the silicide will have dissociated (provided a thick enough amorphous silicon layer is present) and the palladium silicide after SPEG will thus not contain any radioactive silicon atoms (see Fig. 1). An intermediate result could indicate some combination of the two limiting cases.

To determine whether the silicide layer is marked with radioactive silicon or not, samples were etched with aqua regia after solid-phase epitaxial growth of silicon. Aqua regia dissolves palladium silicide readily, but does not attack crystalline silicon, therefore any measured activity in the etchant could only be from the silicide layer. Nevertheless, as a control, blank activated silicon samples (without Pd and amorphous Si), of the same size and origin as the SPEG samples, were also etched in aqua regia and the possible presence of radioactivity in the etchant determined. In Fig. 3 backscattering spectra are shown of a SPEG sample before and after etching with aqua regia. This sample is the same as the one shown in Fig. 2 but it has been heated long enough for all the amorphous Si to be consumed. The position of the front edge of the palladium signal shows that the palladium silicide layer is now on the surface of the sample. The nonuniform nature of the epitaxially grown silicon layer due to island formation in the second stage can be seen from the graded edges of the Pd signal corresponding to the interface between the epitaxially grown Si layer and the palladium silicide layer. The backscattering spectrum of the etched sample still shows the presence of palladium. This is due to the trapping of palladium silicide in the regrown silicon layer during formation and coalescing of the silicon islands.[5]

To determine the amount of silicon radioactivity incorporated initially into the Pd_2Si layer, samples were etched in aqua regia immediately after silicide formation. In these cases, the remaining amorphous silicon was first selectively removed by etching with concentrated HF as it does not attack Pd_2Si or crystalline silicon. Samples were nevertheless first rinsed in distilled water before the final etching with aqua regia to avoid possible radioactive contamination. The silicon radioactivity measured in the Pd_2Si layer after silicide formation served as a reference activity as it should be the same as that expected in the silicide layer after SPEG if the silicide does not dissociate. The reference samples were prepared simultaneously and in exactly the same way as SPEG samples. The activity measured in the etchant from a reference sample as a function of time after the end of the neutron irradiation is given in Fig. 4. Activity measurement usually started about 10 h after activation and it can be seen that the measured activity decays with a half-life of 2.62 h, which is the half-life of ^{31}Si. The decay curve shows that no other radioactivity forms during activation.

Measured radioactivities for four sets of samples having different palladium thicknesses are given in Table I. For each case the thickness of nonradioactive amorphous silicon was greater than that needed to reach the end of the first stage of epitaxial growth. Very little activity is present in the etch from the activated single-crystal blank samples, proving that single-crystal silicon is not soluble in aqua regia. The small amount of activity in cases A and D can probably be ascribed to some soluble contamination of the sample before activation, or to a small piece of solid silicon dislodged from the blank during etching. The reference activity for each case is, as expected, proportional to

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TABLE I. Silicon-31 radioactivity (counts per minute) measured in aqua regia etch solutions. All activities have been normalized to a time corresponding to the end of the neutron activation irradiation. A percentage activity of 0% supports a "dissociation" mechanism, while a value of 100% would confirm a mechanism involving no dissociation of Pd_2Si for solid-phase epitaxial growth of silicon.

	A	B	C	D
Pd thickness (Å)	1335	1379	1735	2425
Si blank activity (cpm)	175	0	0	101
Reference activity in silicide before SPEG (cpm)	7874	9020	12005	15703
Activity in silicide layer after SPEG (cpm)	0	440	0	1128
Percentage activity (%)	0	4.8	0	7.1

the thickness of the original palladium layer. It can be seen from Table I that the amount of radioactivity present in the aqua regia etch from SPEG samples is very much lower than that in the corresponding reference samples. In two cases no radioactivity is found in the silicide layer after SPEG, while in cases B and D only 4.8 and 7.1% of the reference activity is present. If solid-phase epitaxial growth of silicon took place without dissociation of the palladium silicide layer, the activities in the aqua regia etchant from the reference and the SPEG samples would have been the same. It is thus concluded that epitaxial growth of silicon in the Si⟨100⟩/Pd_2Si/Si(a) system takes place by a "dissociation" mechanism. The activities found in aqua regia etch solutions from silicide layers of SPEG samples in cases B and D is possibly due to sample contamination before activation or to trapping of initial palladium silicide during island formation before it has had a chance to dissociate. Such palladium silicide inclusions, if close to the surface area of the sample, could be etched out and thus introduce activity into the etchant solution. In Fig. 5, the activities etched from SPEG (crosses) and reference samples (flagged points) are plotted as a function of Pd thickness. It can clearly be seen that the SPEG activities (crosses) follow the line expected if SPEG takes places by a "dissociation" mechanism.

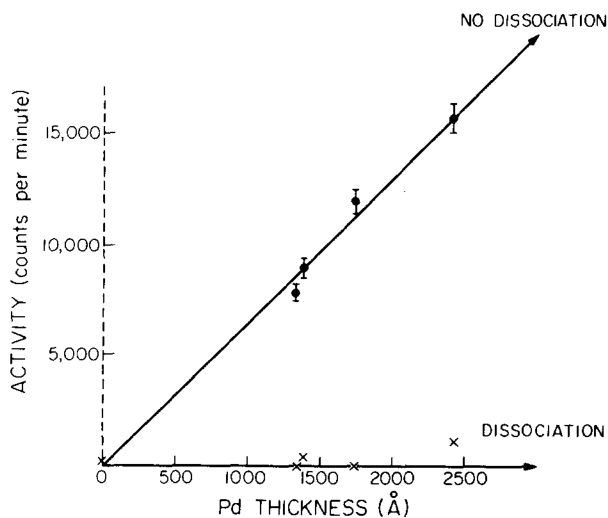

FIG. 5. Activities measured in the silicide layer after initial silicide formation (flagged points) and after SPEG (crosses), as a function of Pd thickness. The SPEG activities (crosses) follow the line expected if epitaxial growth takes place by a "dissociation" mechanism.

TABLE II. Radioactivity measurements for a sample where radioactive silicon was first evaporated onto a nonactivated single-crystal substrate before the subsequent evaporation of palladium and nonactivated amorphous silicon. All activities have been normalized to a time corresponding to the end of the neutron activation irradiation.

Original activity in SPEG sample before etching	4590 ± 280 cpm
Activity in SPEG sample after etching in aqua regia	4370 ± 260 cpm
Activity in aqua regia etchant solution from SPEG sample	590 ± 210 cpm

In the results discussed so far, only the activity in the aqua regia etch solutions was measured, as the amount of radioactive silicon incorporated into the Pd_2Si layer during initial silicide formation is less than 0.01% of the total activity induced in the activated single-crystal substrates during neutron activation. Additional measurements were thus carried out in which approximately 200 Å of radioactive silicon was first evaporated onto nonactivated single-crystal silicon substrates before evaporation of Pd and stable amorphous Si. The Pd thickness chosen was sufficient to use up all the evaporated radioactive silicon during silicide formation. In this case the activity in the SPEG sample itself could be measured before and after etching with aqua regia. These results are given in Table II and also confirm that solid-phase epitaxial growth of silicon in the Si(xtal)/Pd_2Si/Si(amorphous) system takes place by a "dissociation" mechanism, as nearly all the activity remains in the regrown silicon of the SPEG sample after removal of the silicide layer by etching with aqua regia.

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[1]G. Ottaviani, C. Canali, and G. Majni, J. Appl. Phys. **97**, 627 (1976).

[2]H. Sankur, J.O. McCaldin, and J. Devaney, Appl. Phys. Lett. **22**, 64 (1973).

[3]C. Canali, S.U. Campisano, S.S. Lau, Z.L. Liau, and J.W. Mayer, J. Appl. Phys. **46**, 2831 (1975).

[4]S.S. Lau, C. Canali, Z.L. Liau, K. Nakamura, M-A. Nicolet, J.W. Mayer, R.J. Blattner, and C.A. Evans, Appl. Phys. Lett. **28**, 148 (1976).

[5]Z.L. Liau, S.U. Campisano, S.S. Lau, and J.W. Mayer, J. Electrochem. Soc. **122**, 1696 (1975).

[6]W.K. Chu, J.W. Mayer, M-A. Nicolet, T.M. Buck, G. Amsel, and F. Eisen, Thin Solid Films **17**, 1 (1973).

[7]Z.L. Liau, S.S. Lau, M-A. Nicolet, and J.W. Mayer (unpublished).

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