the ion etching process, and at the same time contribute few backscattered electrons to blur the image.

The major limit to resolution at present is the nonuniformity of the metal layer; there is every reason to believe that this problem will be resolved by the use of amorphous metal alloy films with more uniform thickness. If this is the case resolution may be further improved by going to higher electron energies than 45 keV because electron backscattering will be reduced. The electron dose would probably have to be increased in this case, however, because the energy lost to the polymerization process would be reduced.

Finally, the resolution, line sharpness, and wide range of possible structure materials which characterize this process should allow the direct fabrication of many useful devices of which the following are examples: (i) zone-plate lenses or beam collimating apertures with dimensions similar to soft x-ray wavelengths; (ii) x-ray lithographic masks with resolutions comparable to soft x-ray wavelengths and theoretical resist resolutions; (iii) superconducting or semiconductor tunnelling structures with dimensions and spacings comparable to typical tunnelling distances; and (iv) resolution and calibration standards for electron microscopy.

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Dissociation mechanism for solid-phase epitaxy of silicon in the Si ⟨100⟩/Pd_2Si/Si (amorphous) system*

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Solid-phase epitaxial growth (SPEG) of silicon was investigated by a tracer technique using radioactive ^{31}Si formed by neutron activation in a nuclear reactor. After depositing Pd and Si onto activated single-crystal silicon substrates, Pd_2Si was formed with about equal amounts of radioactive and nonradioactive Si during heating at 400°C for 5 min. After a 1-sec annealing stage (450 → 520°C in 1 h) this silicide layer, which moves to the top of the sample during SPEG, is etched off with aqua regia. From the absence of radioactive ^{31}Si in the etch, it is concluded that SPEG takes place by a dissociation mechanism rather than by diffusion.

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It has recently been shown that epitaxial layers of silicon can be grown on a single-crystal silicon substrate from an amorphous silicon layer through palladium silicide by means of solid-state reaction.[1,2] Palladium is evaporated in vacuum onto single-crystal silicon, followed immediately by the deposition of amorphous silicon. During the first annealing stage (between 200 and 400°C), the Pd reacts with both the substrate and the amorphous layer, forming Pd_2Si. During the second annealing stage at a higher temperature (about 500°C), Si grows epitaxially on the substrate. The process stops when all the amorphous Si has been consumed and the silicide layer appears on the surface of the sample. The driving force for the amorphous-to-crystalline transition is thought to be the higher free energy of the amorphous material as compared to the crystalline form.

Two possible mechanisms can be postulated for solid-

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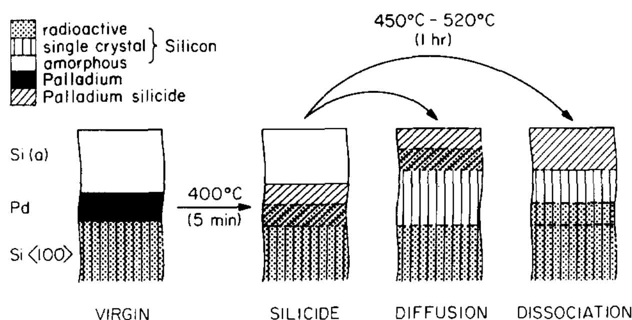

FIG. 1. Schematic diagram showing how radioactive Si can be used to distinguish between a dissociation or a diffusion mechanism for SPEG of Si. The presence (or absence) of radioactive Si in the top silicide layer is determined by beta counting after etching the silicide off with aqua regia.

phase epitaxial growth (SPEG) of silicon in this system. Silicon from the amorphous phase can diffuse through the silicide layer ("diffusion" model) and recrystallize on the single-crystal substrate epitaxially. In this case the silicide layer only acts as a medium for the Si transport, similar to the Si(xtal)/Al/Si(a) system.[3] On the other hand, the Pd_2Si layer can dissociate to provide silicon at the single-crystal interface while new silicide is formed at the interface with the amorphous silicon ("dissociation" model). In this case the Pd_2Si layer plays an active role in the transport of Si. To determine which of these models is applicable, a tracer experiment using radioactive silicon was carried out.

Commercially available single-crystal silicon wafers with polished surfaces and ⟨100⟩ orientation were first cleaned and then irradiated in a Triga nuclear reactor. The only relatively long-lived radioactivity formed from silicon during neutron activation is ^{31}Si by the reaction $^{30}\mathrm{Si}\,(n,\gamma)\,^{31}\mathrm{Si}$. This isotope is a beta emitter decaying with a half-life of 2.62 h and can readily be measured. About 1000 Å of Pd was then deposited onto these activated substrates by electron-gun evaporation followed immediately by the deposition of approximately 3500 Å of amorphous nonradioactive silicon. Samples were then first annealed at 400°C for 5 min for silicide formation. Rutherford scattering with 2-MeV alpha particles showed that the Pd usually reacted with equal amounts of activated single-crystal silicon substrate 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 the epitaxial growth of silicon.

If SPEG proceeds by diffusion, one-half of the silicide which has moved to the surface of the sample will still be marked with radioactive silicon atoms (see Fig. 1). However, if SPEG proceeds by dissociation, all the silicide will have dissociated (provided a thick enough amorphous silicon layer is present) and the palladium silicide after annealing will thus not contain any radioactive silicon atoms. An intermediate result could indicate some combination of the two limiting cases.

To determine whether the silicide layer after SPEG is marked with radioactive silicon or not, samples were etched in aqua regia after the second annealing stage. Aqua regia does not attack crystalline silicon but dissolves the silicide layer readily. After drying the etchant solutions with infrared lamps the presence of beta radioactivity from ^{31}Si was determined by measurement with an end-window Geiger-Müller detector. Drying had to be carried out before activity measurement to avoid absorption losses in the solvent. To monitor the epitaxial growth and etching processes quantitatively, 2-MeV ^{4}He backscattering spectrometry was used.[4] 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.

Another set of reference activity measurements was performed by etching the radioactive Pd_2Si after the first annealing stage for silicide formation. In these cases, the amorphous silicon was first removed by etching with concentrated HF. Both crystalline silicon and Pd_2Si are not attacked by HF, but reference samples were nevertheless first rinsed in distilled water before the final etching with aqua regia to avoid possible radioactive contamination. The control blank and reference samples were always prepared simultaneously with the SPEG samples.

Measured radioactivities for two different sets of samples are given in Table I. Very little activity is present from the blank radioactive single-crystal silicon substrate. The small amount of activity in case B 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 from samples etched after silicide formation only is proportional to the thickness of the original evaporated Pd layer. A Pd thickness of 1335 Å was used in both cases given in Table I. Hardly any activity is present in the aqua regia etch from the SPEG samples. The small amount of activity in case A is of the same order of magnitude as that from the Si blank sample. If the SPEG of silicon took place by silicon diffusion (diffusion model) through the palladium silicide layer, the activities of the reference and of the SPEG samples would have been the same. Because only 2.4% and 0% of the reference activity is present in the silicide after SPEG, it is concluded that epitaxial growth of silicon in this system takes place by a dissociation mechanism.

TABLE I. ^{31}Si radioactivity (counts/min) 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 diffusion mechanism for SPEG of silicon.

Etch solution	Case A	Case B
Si blank	0 counts/min	175 counts/min
Pd_2Si before SPEG	7820 counts/min	7927 counts/min
SPEG	190 counts/min	0 counts/min
Percentage	2.4%	0%

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Enhanced crystallinity of silicon films grown from eutectic melt on aluminum sheets

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Silicon films were grown from Al-Si eutectic melt directly formed on aluminum sheets. High-energy silicon atoms were deposited onto aluminum sheets at 420°C in an argon discharge atmosphere of 5×10^{-4} Torr using an rf ion-plating system. A significant increase in the crystallinity of silicon films was observed from transmission electron diffraction studies. The mechanism of silicon eutectic growth on aluminum sheets is also discussed.

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This letter reports a new method for growing polycrystalline silicon films with a significant increase in crystallinity on aluminum sheets. The use of polycrystalline Si films with a nominal thickness of $5\sim10$ μm is considered as a promising approach for the fabrication of low-cost solar cells for terrestrial applications.[1,2] However, films of this thickness require suitable substrates. These substrates should be low cost. Therefore, many studies have been made, aimed at producing polycrystalline Si films on low-cost substrates.[1–3] Although aluminum sheets are one of the most promising low-cost substrates, the melting point of Al and the eutectic point of the Al-Si system are low, 660 and 577°C, respectively. Therefore, Si has to be deposited onto Al substrates below the eutectic temperature of 577°C to obtain Si films. However, the crystallinity of Si films deposited at such a low temperature is generally very poor. Some interesting aspects of eutectic growth of Si have been discussed by Li.[4] Chang *et al.* have demonstrated that the crystallinity of Si films deposited onto fused quartz had significantly increased when Si films were grown from the Al-Si eutectic melt at fairly low temperatures.[5] However, fused quartz is very expensive. Therefore, an alternate metal substrate, Al, and a new method of eutectic growth of Si on Al substrates was considered.

An illustration of the eutectic growth mechanism of Si films on Al substrates is as shown in Fig. 1. When high-energy particles (atoms or ions containing Si) are deposited onto the surface region of an Al substrate, most of the energy of particles is given up in the form of heat. This means that the bulk of the Al substrate may be kept at low temperature while the surface may be very hot, depending on the thermal transport prop-

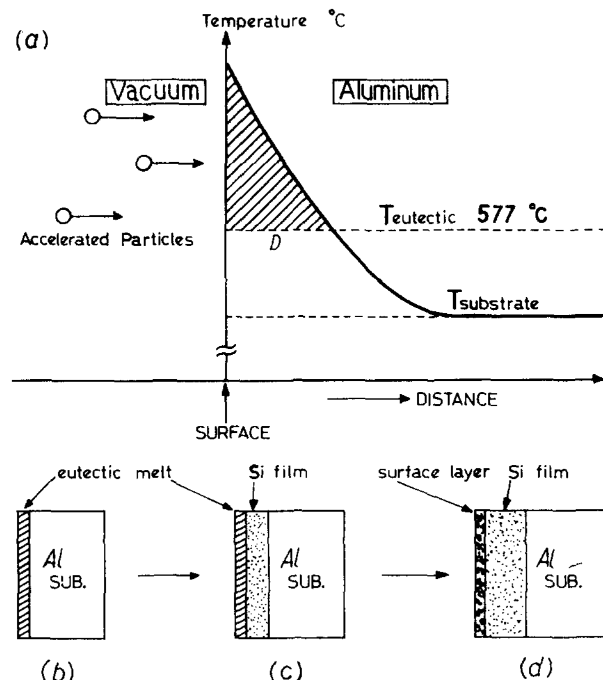

FIG. 1. Si film eutectic growth mechanism on Al substrate: (a) growth mechanism, (b) just after the beginning of the growth, (c) during the growth, (d) after the growth.

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