Formation of submicron epitaxial islands of Pd_2Si on silicon

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It has been found that annealing Pd-Er deposits on a (001) silicon surface results in the formation of isolated submicron islands of Pd_2Si with two epitaxially oriented habits. By contrast, when Pd is annealed on a (111) silicon substrate, Pd_2Si is formed with full coverage and a specific epitaxy.

When Pd is deposited on (111) silicon and annealed, Pd_2Si is formed epitaxially with full coverage[1] and a well defined interfacial structure[2] as has been characterized by transmission electron microscopy (TEM) (e.g., Refs. 3 and 4). The reaction on (001) oriented silicon can, however, result in island formation[5] and this is of considerable technological interest. In this letter we describe the morphology and orientation relationship of the submicron Pd_2Si islands which grow into (001) silicon when Pd-Er deposits are annealed. We also report the way the interfacial reaction can result in the formation of an amorphous intermediate layer between the islands and an originally microcrystalline deposit. A deposit containing 25% Er was chosen for the investigation of the reaction not only to dilute the Pd but also because it appears that low-temperature Si interaction is promoted, the Er reacting with any native oxide on the substrate.

The Pd-25% Er alloy was deposited onto *p*-type (001) silicon substrates to a thickness of approximately 70 nm using the method described by Ottaviani *et al.*[6] The Pd and Er were electron beam co-deposited at 1 nm/s deposition rate in a vacuum of 10^{-5} Nm^{-2}. Samples were examined by cross-sectional and plan-view TEM as deposited and after annealing for 1 h at 620 K in a furnace flushed with purified helium. The TEM foils were prepared using the methods described by Newcomb *et al.*[7] The cross-sectional specimens allowed the morphology and depths of the interaction products to be examined directly, while phase identification was achieved more easily using plan-view specimens, since these contained larger volumes of thin material from a given position relative to the interface.

The middle of the Pd-Er layer as deposited on silicon is shown in plan view in Fig. 1 and is representative of the Pd-Er adjacent to the substrate. This was confirmed by the examination of different regions in plan view from different depths relative to the interface. The Pd-Er in these regions was of a predominantly microcrystalline morphology with a grain size of about 4 nm, although diffraction patterns [such as Fig. 1(b)] gave some evidence for a small volume fraction of either amorphous or still smaller microcrystalline material. Nearer the outer surface of the Pd-Er deposit, erbium oxide (Er_2O_3) is also formed as is again apparent from Fig. 1(b) and the larger grain size of this oxide than the Pd_3Er, as suggested by the diffraction pattern, was confirmed by dark

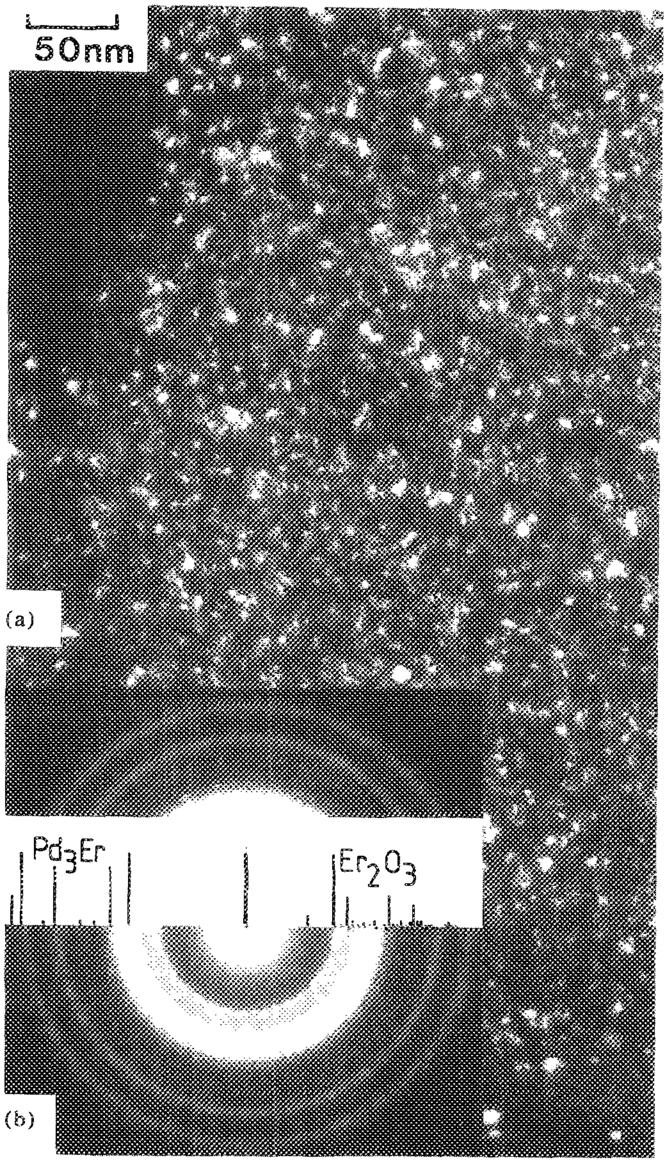

FIG. 1. (a) Plan-view TEM dark field image and (b) diffraction pattern from the middle of the Pd-Er layer on Si before annealing. The positions of the Pd_3Er (continous diffuse) and Er_2O_3 (less continuous but sharper) rings are shown in (b).

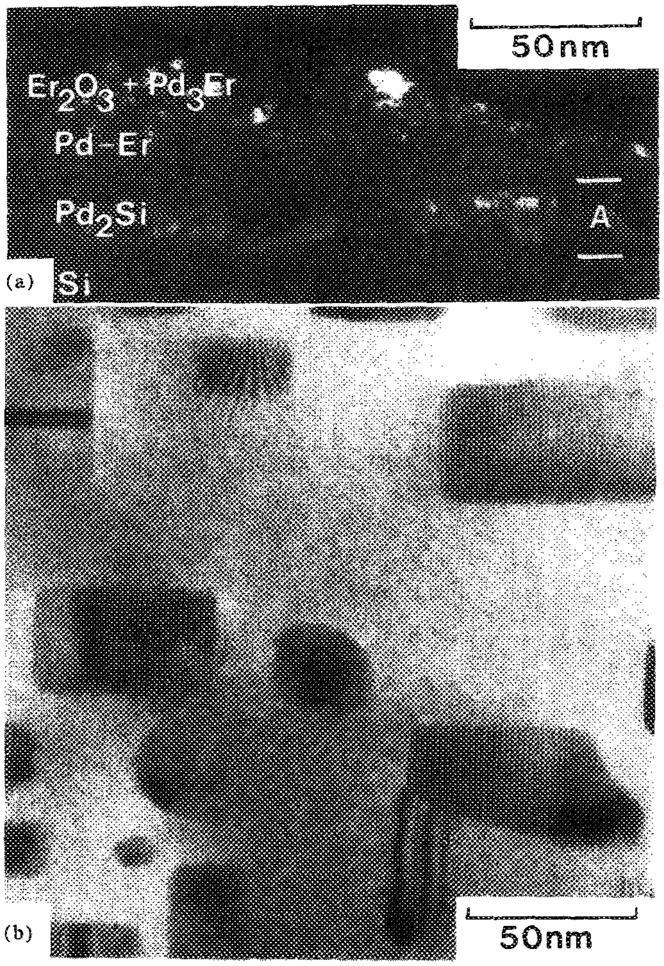

FIG. 2. Pd-Er|Si after annealing for 1 h at 620 K. (a) Dark field cross-sectional image showing the amorphous layer adjacent to the Pd-Er|Si interface and the Pd_2Si crystals which have grown from the Pd-Er|Si interface into the substrate. (b) Bright field plan view from region A in (a) showing the two habits of the Pd_2Si crystals. The epitaxial nature is indicated both by the diffraction pattern from this region in Fig. 3(a) and by the moiré patterns formed from interference of the 0002 Pd_2Si and 220 Si reflections for the islands aligned left to right.

field examination. No evidence was obtained, however, for a reaction between Pd-Er and Si at room temperature using either cross-sectional or plan-view TEM.

The microstructure after annealing for 1 h at 620 K is shown in cross section in Fig. 2(a). The outer surface layer of the Pd-Er is unchanged for this annealing temperature but the Pd_2Si crystals can now be seen to have grown from the Pd-Er|Si interface into the substrate. The Pd-Er adjacent to the Si has also now become amorphous. The formation of this amorphous layer has been shown[8] to be correlated with the diffusion of Si into the Pd-Er. The region from just into the amorphous layer above the Pd-Er|Si interface to below the Pd_2Si crystals in the Si [region A in Fig. 2(a)] is shown in plan view in Fig. 2(b). The isolated nature of the Pd_2Si islands is clear, as are their two distinct habits on the (001) Si substrate.

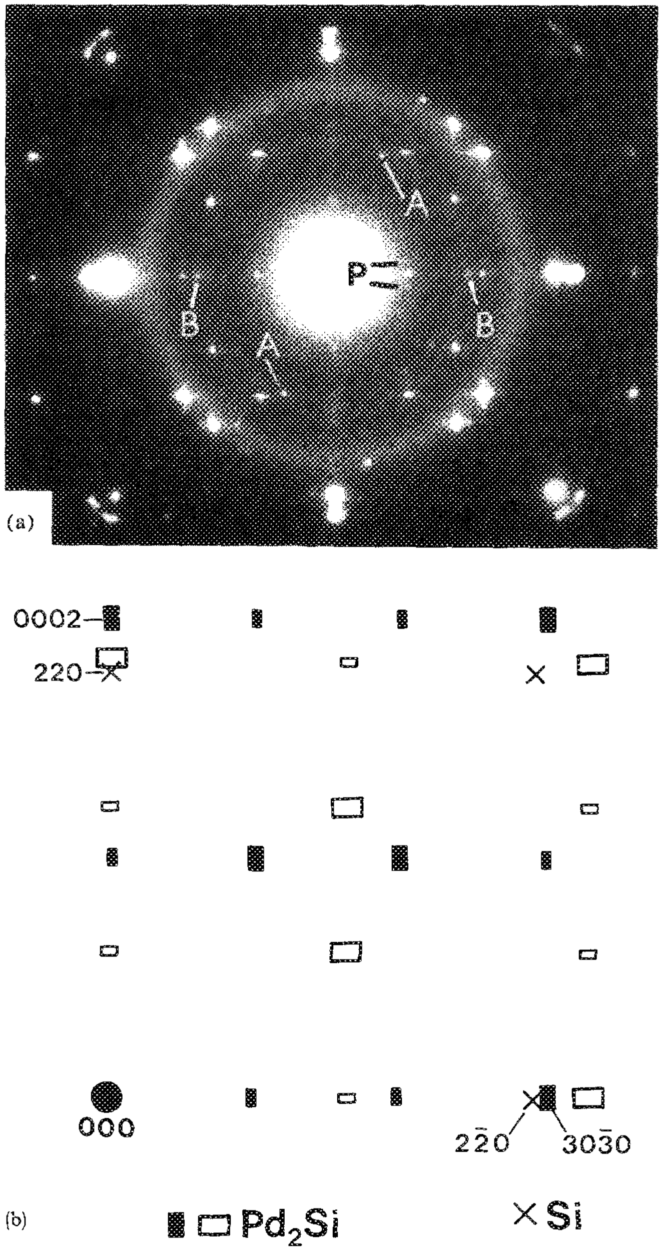

FIG. 3. (a) (001) Si diffraction pattern from the region shown in Fig. 2(b). The main reflections from the two epitaxial Pd_2Si island familes are indexed in the diagram in (b), which shows the top right quarter of (a).

The epitaxial relationships of the Pd_2Si to the Si are further demonstrated by the diffraction pattern taken with (001) Si parallel to the beam shown in Fig. 3(a). A good fit for Fig. 3(a) was obtained using a unit cell for Pd_2Si with $a = 0.6493$ nm and $c = 0.3427$ nm and it should be noted that none of the extra reflections that might be expected for the larger unit cell structure described by Nylund[9] was observed. A diagram of the diffraction pattern is shown in Fig. 3(b) where the two main families of Pd_2Si reflections for the two island orientations are differentiated (by ▮ and ▭). The strong reflections of the type $20\bar{2}1$ for these islands are streaked in the $[10\bar{1}0]$ direction as a result of facets on the islands and also exhibit pairs of extra reflections on either side of them in the [0001] direction. These extra paired reflections are repeated at the $h0\bar{h}0$ reflections [P on Fig. 3(a)] and when the islands are viewed in dark field in any of these reflections their contrast is modulated in a nearly regular manner, related to the separation of the pairs of spots.

High-resolution cross-sectional micrographs of the islands also exhibit a regular dislocation array aligned in the $[10\bar{1}0]$ direction in the $Pd_2Si|Si$ interface. The only other reflections in Fig. 3(a) with which we need be concerned, and which are not the result of double diffraction, are arrowed. The isolated reflections (A) have a good fit with $\{11\bar{2}0\}Pd_2Si$ and apparently have their origin in a nonepitaxial island but the reflections marked B between the 0001 reflections of one family and the $20\bar{2}0$ reflections of the other have not been satisfactorily indexed.

The orientation relationship between the Pd_2Si crystals and the (001) Si substrate was thus deduced to be $(2\bar{1}\bar{1}0)Pd_2Si\|(001)$ Si with either [0001] $Pd_2Si\|[110]$ Si or [0001] $Pd_2Si\|$ $[1\bar{1}0]$ Si. This differs from the orientation relationships which result when Pd alone is deposited and annealed on any of the (001), (110), or (111) Si substrates.[2,10] In these cases [0001] Pd_2Si is always found to be parallel to the substrate normal with $[01\bar{1}0]$ Pd_2Si parallel to $[1\bar{1}0]$ Si. The reason for the $[01\bar{1}0]$ direction in Pd_2Si tending to be parallel to the $[1\bar{1}0]$ Si is that the misfit between $(03\bar{3}0)$ Pd_2Si and $(2\bar{2}0)$ Si is relatively small (0.03). This allows the particularly good epitaxy associated with (111) Si,[11] for which the three $\langle 01\bar{1}0\rangle$ Pd_2Si directions can all match well with the three $\langle 110\rangle$ directions in the plane of the substrate. However, the reason for the Pd_2Si [0001] direction being parallel to the substrate normal for all three substrates is more likely to be because Pd_2Si grows much faster during annealing along the [0001] direction. This is further supported by the fact that when Pd is deposited onto an amorphous Si substrate and annealed, Pd_2Si still grows with its [0001] direction perpendicular to the substrate surface.[10,12]

When Pd_2Si grows at the Pd-Er|Si interface a Pd_2Si $[01\bar{1}0]$ direction is again parallel to $[1\bar{1}0]$ Si, but now [0001] Pd_2Si lies in the plane of the substrate, rather than being normal to it as when Pd_2Si is grown from a pure Pd deposit. The change in orientation relation suggests kinetic control of the interaction: with an alloyed and "diluted" deposit, the Pd_2Si crystals are aligned so that their fastest growth direction, [0001], lies in the Pd-Er|Si interface, thus minimizing the distance that Pd and Si have to diffuse during growth. The preferential growth of Pd_2Si along [0001] is also supported by the elongation of the Pd_2Si crystals along the [0001] direction despite the misfit with [110] Si in this direction being 0.11, while that of Pd_2Si $[01\bar{1}0]$ to $[1\bar{1}0]$ Si is only 0.03.

The large misfit between [0001] Pd_2Si and [110] Si has resulted in many of the Pd_2Si crystals in Fig. 2(b) being highly strained as viewed in the thin foil. This is shown both by the variations in the spacing of the 0002 Pd_2Si/220 Si moiré fringes in some of the smaller crystals and by the closely spaced bend contours present on many of the larger crystals. While the fact that the amorphous Pd-Er-Si is formed during the interaction above the Pd_2Si islands and immediately adjacent to the original Si interface [see Fig. 2(a)] is of interest in its own right, here we may take this to provide further evidence for the kinetic control of the interaction.

In conclusion, we note that the formation of nanometer sized Pd_2Si particles in Si has application, given a method to link these islands controllably, in providing submicron conducting pathways. It should be possible to deposit patterns of Pd-Er using electron beam lithography, reaction nucleation being promoted by an ion beam exposure, so that annealing would allow Pd_2Si islands to grow and link together. The metallic lines of Pd_2Si could then be isolated in the Si by etching off the remaining Pd-Er so that Si could then even be deposited, possible epitaxially, over the whole pattern.

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