

ION- AND ELECTRON-BEAM INDUCED REACTIONS IN MICROCRYSTALLINE Pd₃Er

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Introduction

Microcrystalline alloys of Pd-Er can undergo complex and interesting interactions when annealed on Si. The alloy, a combination of a near noble and a rare earth metal, can form either Pd₂Si or ErSi₂ which have similar formation energies. There are a number of ways of determining which silicide is formed and Ottaviani et al. (1) have, for example, demonstrated that the different Schottky barrier heights of the two silicides can be used to distinguish the one from the other. It is Pd₂Si which is formed when Pd rich alloys are annealed on Si and the morphology and chemistry of the various interactions which occur for Pd₇₀Er₃₀ on Si have been investigated in detail using transmission electron microscopy (TEM) (2). The silicide is formed as epitaxially strained islands which grow down into the silicon with a flat upper face at the original Pd-Er/Si interface. Silicon has also been shown to diffuse up, concurrently, into the Pd-Er during annealing with the resultant formation, presumably under kinetic control, of an amorphous Pd-Er-Si zone between the silicide islands and the unreacted microcrystalline Pd₃Er above this (3). Amorphisation interactions of this type have to be treated with considerable caution given the danger that the methods of TEM specimen preparation used (4), which invariably involve ion beam thinning, can influence the observations: it has, for example, been shown that a 3 kV argon ion beam can itself induce a silicide reaction when directed through a thin Pd-Er layer into the silicon substrate (2,5).

We describe here the results of an investigation which was originally intended to differentiate between the amorphous phases produced as a result of ion beam thinning and by interdiffusion between the Si substrate and superposed microcrystalline Pd₃Er. In the former category of processes we included the increased propensity of a material such as Pd₃Er to form amorphous oxide on exposure to air after ion irradiation. We have, however, found that the Pd-Er can undergo both ion- and electron-beam induced reactions and discuss these as of interest in their own right.

Materials and Methods

The Pd₇₀Er₃₀ alloy examined was prepared as described elsewhere (1) by electron beam codeposition on a (100) Si substrate to a thickness of approximately 140 nm. "Plan-view" TEM specimens were prepared by 5 kV argon ion milling at an angle of 20° using a liquid N₂ cooled stage on a Gatan ion beam miller and standard techniques (4). The areas of foil described here were from thickness zones at and near to the upper surface of the original Pd-Er deposit and thus well away from the silicon interface. Amorphisation by interdiffusion was thus precluded as was the silicide reaction promoted at the interface by the thinning process. Areas from the centre of the original Pd₇₀Er₃₀ were also examined and found to behave in a similar manner to those at the upper surface. A Philips 400T electron microscope operated at 100 kV was used for the microscopy.

Results

Electron diffraction patterns obtained from a relatively thick area of the specimen and from a thin region near to the foil edge may be compared in Figs.1a and b. The former is typical of a microcrystalline Pd₃Er alloy, and dark field techniques were used to demonstrate that the material was indeed microcrystalline: the images of grains seen using the innermost and strongest Pd₃Er ring were between 2 and 6 nm in size (see fig.3a). The diffuse halo inside the strong Pd₃Er ring in the diffraction pattern obtained from the edge of the foil (fig.1b) is much less visible in the pattern dominated by diffraction from

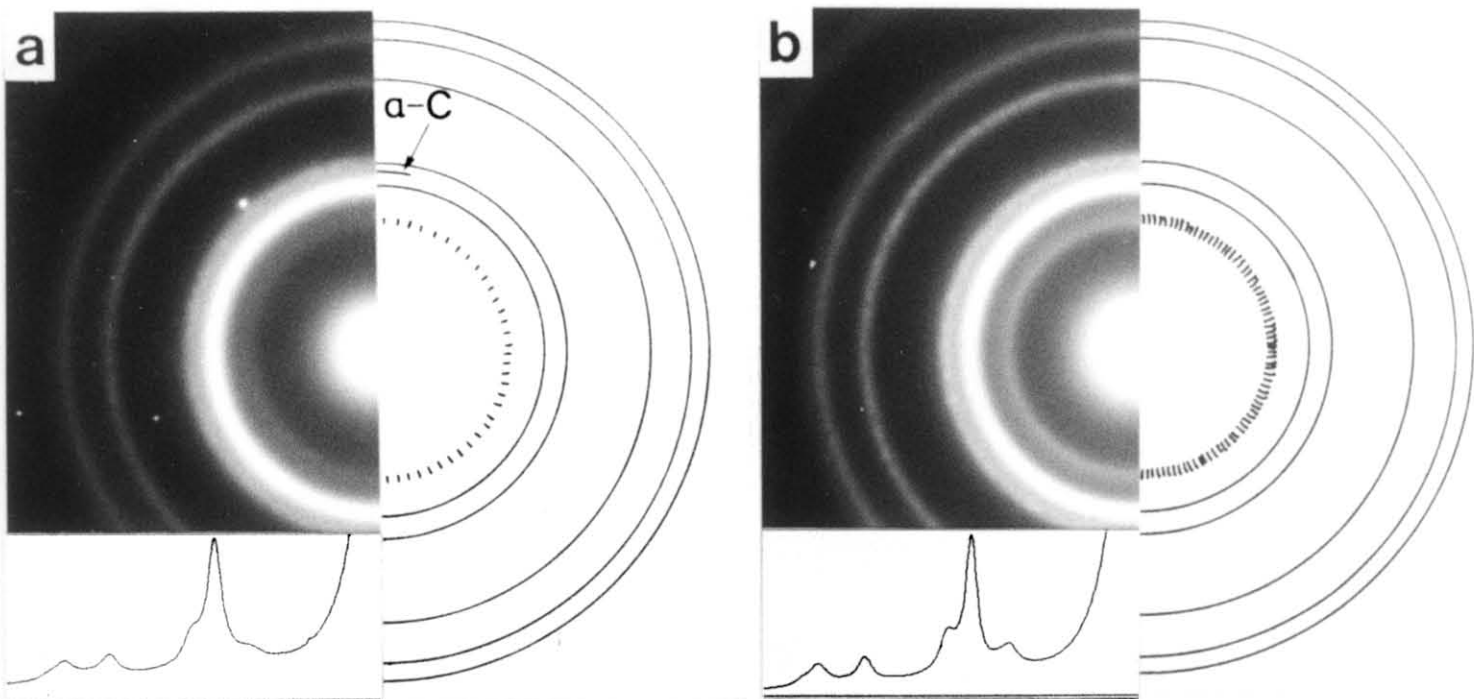


FIG.1. Electron diffraction patterns with inset densitometer traces from a) thick and b) thin Pd-Er after ion beam thinning. The inner diffuse halo, stronger in b), is associated with an ion beam induced surface amorphisation. The discretediffraction spots in a) come from a region of silicon substrate well away from the area shown in figure 3.

the bulk alloy (fig.1a), indicating that this ring has its origin in a surface layer on the foil. This inner halo is not associated with amorphous Pd-Er which exhibits a broadened first halo much nearer to the position of the strong Pd₃Er ring used for imaging the microcrystalline material. Equally the innermost halo has its origin in neither carbon contamination (the position for amorphous C diffraction is marked on fig 1a), nor ion-beam sputter deposits. Such sputter deposits are normally microcrystalline Pd₃Er, and can otherwise be precluded by EDX analysis (as proved necessary).

A dark-field micrograph, obtained using this inner halo, of a thin region near the foil edge is shown in fig.3b. The objective aperture size for this image gave an Airy disc size of ~1 nm and the dark field "speckle" is generally consistent with this. There is some speckle (eg.A) smaller than the aperture limit, while speckles larger than the Airy disc (eg.B) generally show the correlations typical of the dark field scattering of amorphous material (5). That the speckle is objective aperture limited in size within the above limitations is a good test for a material being amorphous (6). However in some regions,

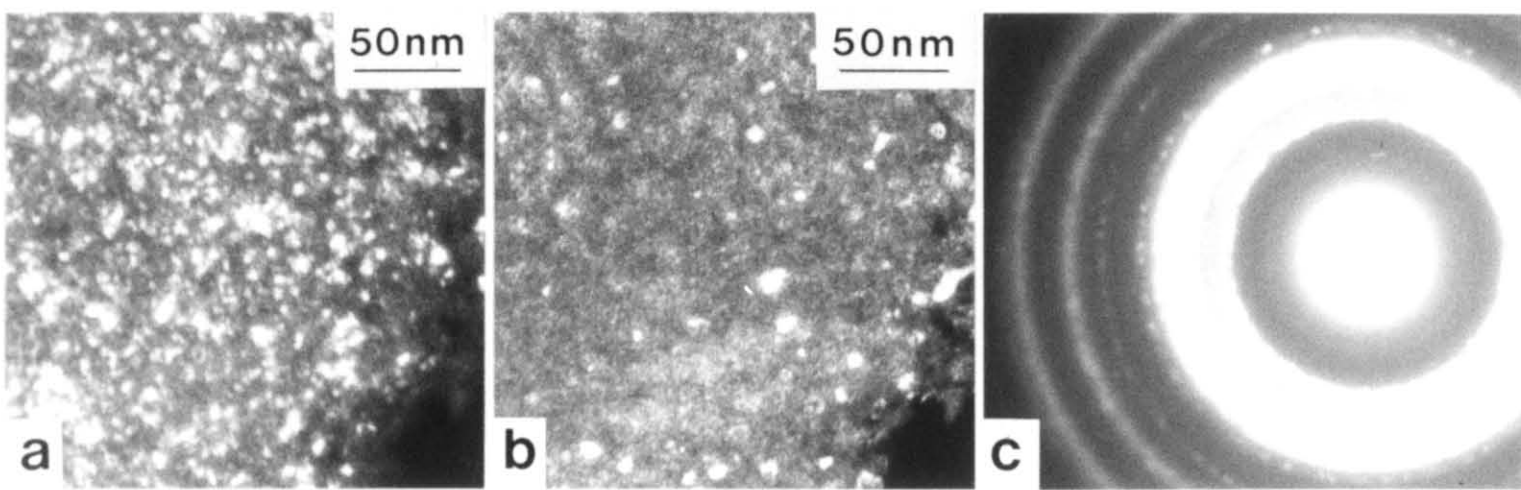


FIG.2 Dark field images from Pd-Er, after prolonged exposure to air, using electrons diffracted into a) the strong inner Pd₃Er ring and b) the innermost erbium oxide ring visible in the diffraction pattern c). The microcrystalline oxide in b) should be compared with the amorphous oxide resulting from ion irradiation shown in fig.3b.

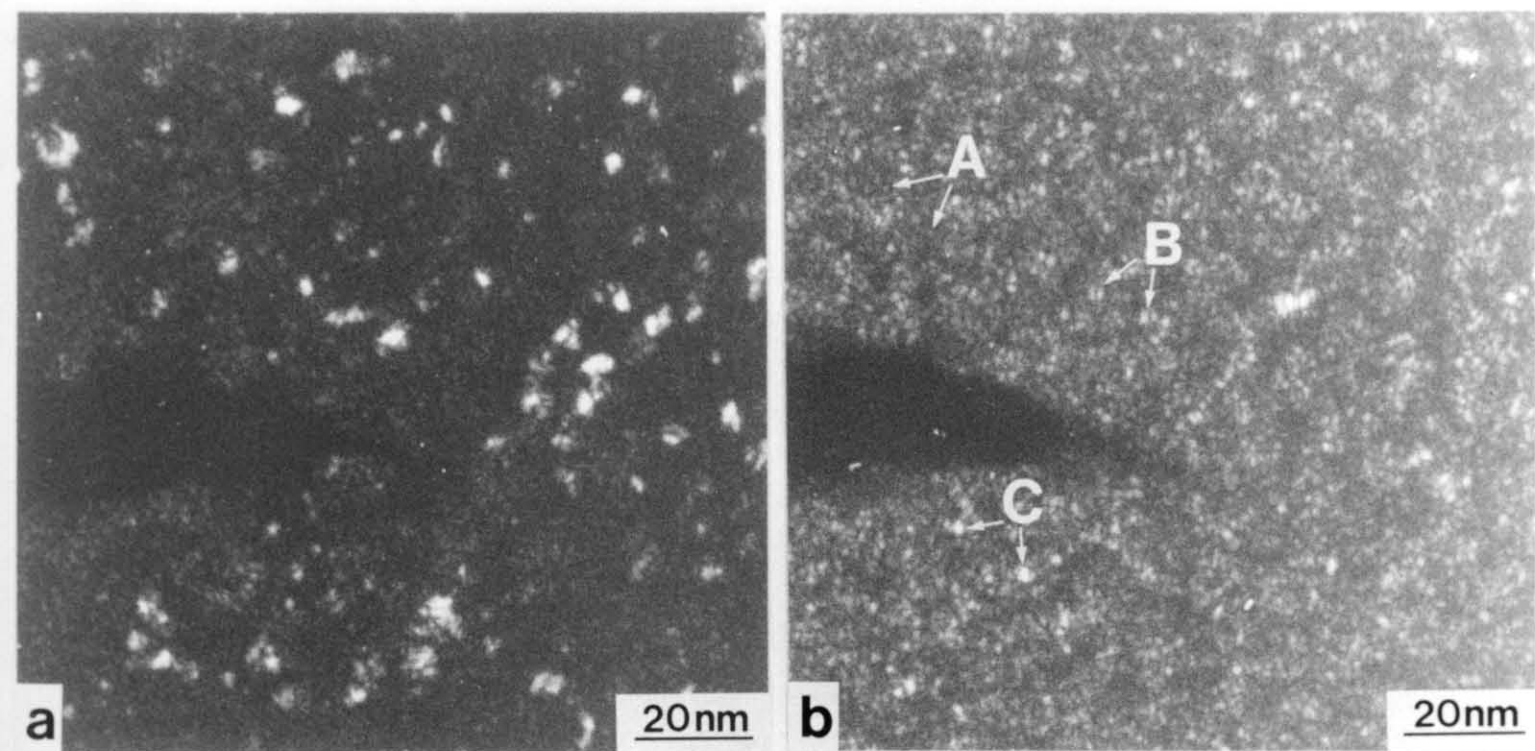


FIG.3. Dark field images using electrons diffracted into a) the strong inner Pd_3Er ring and b) the diffuse inner halo. b) exhibits the aperture limited speckle characteristic of amorphous materials with speckle smaller than the aperture limit visible as at A and larger as at B. Some microcrystallites are also present as at C.

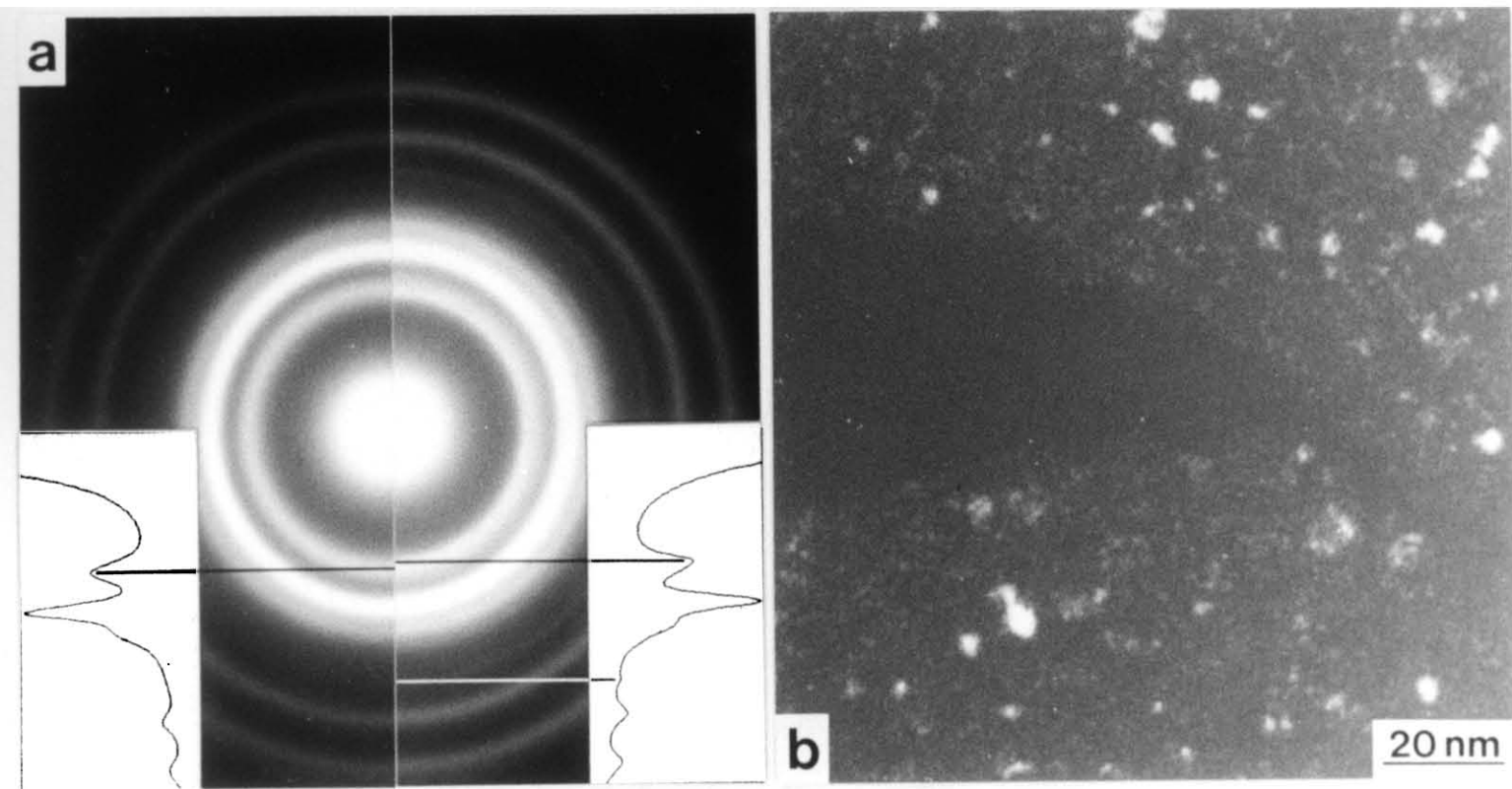


FIG.4. a) Electron diffraction patterns with inset densitometer traces from the same region as fig.3 a and b taken before (left) and after (right) a period of electron irradiation in the microscope. After irradiation, diffraction rings indicative of a microcrystalline material appear, as marked. This microcrystalline substance is shown in dark field in b) using electrons diffracted into the inner ring (and halo) as for fig.3b.

such as those marked C in fig.3a, the speckle intensity suggests possible partial microcrystallinity with a size of ~ 0.8 nm, the limit at which an electron microscope can be used to make such a differentiation. An interesting feature of the contrast from the amorphous surface material is that it appears to be heterogeneous, exhibiting patchiness on a scale of about 10 nm, though the form of the heterogeneity is difficult to characterise given that both surfaces of the foil are imaged. It was, however, demonstrated that this effect was not associated with either the morphology or size of the matrix microcrystalline Pd_3Er grains as can be seen by comparing fig.3b with the dark field image of the same region as that shown in (fig.3a) obtained using the first Pd_3Er ring. The patchiness of the contrast is suggestive of an association with the surface roughness typically developed during ion-beam thinning which results in localised regions of greater and lower ion beam penetration for the low angle of ion beam incidence used.

Specimen areas of the type described may be reexamined with no change in appearance after several hours exposure to air at room temperature. We should also note that Pd-Er films will form an erbium oxide after very prolonged exposure to air at room temperature ($\sim 10^6$ - 10^7 s), but that the oxide formed under such circumstances is microcrystalline see fig.2 (5). We can thus be clear that the amorphous erbium oxide surface layers discussed above are formed either during ion beam irradiation or on subsequent air exposure as a result of the sensitisation of the Pd-Er film to O_2 oxidation caused by ion beam damage. However, at a typical microscope pressure of 10^{-3} Pa, exposure of a specimen with an amorphous erbium oxide surface layer to a normal beam current for no more than half an hour results in a further surface reaction. The diffraction patterns shown in fig.4a were obtained from a thin region before and after such a period of observation in the microscope. The sharpening of the halo and the appearance of new, sharper rings is indicative of crystallisation. This was further demonstrated by the comparison of a dark field image obtained using the innermost diffracted ring and halo (fig.4b) with a similar image of the same region obtained prior to the electron beam induced interaction using the inner halo (figure 3b). Electron energy loss spectroscopy was used in an attempt to determine whether or not oxygen was incorporated as a result of the ion beam induced amorphisation. While this is a reasonable assumption, the proximity of the Pd M_3 edge to the oxygen K edge prevented us from eliminating the possibility that the original Pd-Er alloy contained the small amount of oxygen which was observed. The position of the amorphous halo is in fact consistent with it being associated with an erbium rich oxide based on Er_2O_3 but the crystalline phase formed during the electron beam irradiation, at a grain size of about 5 nm (fig.4b), has a measured d spacing some 3% larger than published data (7). It is difficult to judge whether or not the inner amorphous halo in the diffraction pattern and the speckle contrast associated with this are simultaneously weakened after electron bombardment (both certainly remain visible), but the oxide crystallisation does not seem to be related to the surface patterning of the amorphous regions whose formation we have associated with the ion beam milling.

Conclusion

It is clear that considerable care is required in order to differentiate the various types of surface interaction which can occur for the Pd-Er and Pd-Er/Si system. We may however conclude that the interactions described here for Pd-Er are distinguishable from those caused by interdiffusion for Pd-Er/Si (2,5). We have also demonstrated that a low voltage (5 kV) argon ion beam can promote amorphisation with the incorporation of oxygen and further that an 100 kV electron beam can accelerate this materials' crystallisation.

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