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# Phase formation by ion beam mixing in Ni/Al, Pd/Al, and Pt/Al bilayers

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Ion beam and thermal reactions in thin-film bilayers of Ni/Al, Pd/Al, and Pt/Al have been investigated using electron diffraction and Rutherford backscattering (RBS). Ion mixing was performed with 600-keV Xe ions at room temperature with doses ranging between  $0.25$  to  $12 \times 10^{15}$  ions/cm<sup>2</sup>. The compositions of the ion induced crystalline phases, NiAl and PdAl, differ both from the overall atomic compositions of the ion mixed layers (as determined by RBS) and from the compositions of the layers obtained by thermal annealing. In Pt/Al bilayers ion mixing forms an amorphous region with atomic composition Pt<sub>40</sub>Al<sub>60</sub> while thermal annealing shows the formation of crystalline Pt<sub>2</sub>Al<sub>3</sub>. We believe that actual crystal compound formation during mixing is dependent on the high quench rate in the collision cascade region.

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Ion beam and thermal reactions in thin-film silicides have undergone extensive investigation during the past several years.<sup>1-3</sup> Experimental findings showed that the initial reactions in both processes resulted in identical compound formation in most silicide systems. Observation of the composition of the reacted layer indicated that the first ion induced mixture and the first thermal compound were nearly identical. Also, x-ray diffraction measurement confirmed the presence of ion induced crystalline phases whose compositions were in good agreement with that found with Rutherford backscattering spectroscopy (RBS) analysis.<sup>4</sup>

In the present work we have investigated the formation of Al intermetallic compounds formed by ion beam mixing of metal/Al thin-film bilayers of Pd/Al, Ni/Al, and Pt/Al. The results of this experiment indicate that the first ion induced and thermal crystal compounds in these bilayers are not well correlated, which is in sharp contrast to silicide bilayer reactions. Also in contrast to the silicide findings, we find in ion reacted Al bilayers that the atomic composition of the reacted layer differs from the composition of the crystalline compound observed by electron diffraction.

Samples were prepared by sequential deposition in an oil-free vacuum system. Pressures during deposition were about  $8 \times 10^{-7}$  Torr. Transmission electron microscopy (TEM) samples were prepared by deposition of layers of Al and near-noble metal onto NaCl which was later dissolved away in de-ionized water. The metallic thin-film couple was then placed on copper TEM grids for further processing and examination. Samples which were to be analyzed by RBS were deposited on SiO<sub>2</sub> substrates and in the Pd/Al and Pt/Al systems a prelayer of Ni was first deposited to allow energy separation of the Al and Si RBS signals.

Ion mixing was carried out at room temperature in a vacuum better than  $1 \times 10^{-6}$  Torr. Samples were either bilayer couples on TEM grids or SiO<sub>2</sub> substrates. Energetic Xe ions of 600 keV were employed with doses ranging from  $2.5 \times 10^{14}$  to  $1.2 \times 10^{16}$  ions/cm<sup>2</sup>. Ion currents measured at the sample were maintained at  $0.5 \mu\text{A}/\text{cm}^2$  or below in an attempt to minimize beam heating effects. Thermal treatments were carried out *in situ* using a TEM heating stage in a

vacuum better than  $10^{-6}$  Torr. TEM work was performed on a JEOL 200 CX.

After Ni/Al bilayers were subjected to Xe irradiation, RBS analysis revealed a step in the spectra (Fig. 1) which indicated a composition of Ni<sub>25</sub>Al<sub>75</sub>. When ion mixed samples were examined by electron diffraction [Fig. 2(a)] it was found that the only ion induced crystalline compound present was NiAl. Diffraction confirmed the presence of this intermetallic compound at doses ranging from  $1 \times 10^{15}$  to  $12 \times 10^{15}$  ions/cm<sup>2</sup>. At a dose of  $\sim 6 \times 10^{15}$  ions/cm<sup>2</sup> a diffuse band appeared in the diffraction pattern indicating the presence of an ion induced amorphous phase [Fig. 2(a)]. Both the amorphous and NiAl phases were observed by diffraction up to the maximum dose.

Electron diffraction patterns taken during the *in situ* annealing of as-deposited Ni/Al bilayers revealed the presence of NiAl<sub>3</sub> after 10 min at 250 °C [Fig. 2(b)]. This phase differs from the ion mixed crystalline compound NiAl but agrees with that found previously<sup>5</sup> in the Al/Ni bilayers at temperatures of 200–300 °C.

Ion mixing was found to be more efficient (a factor of 5–10 smaller dose is required) in Pd/Al and Pt/Al bilayers

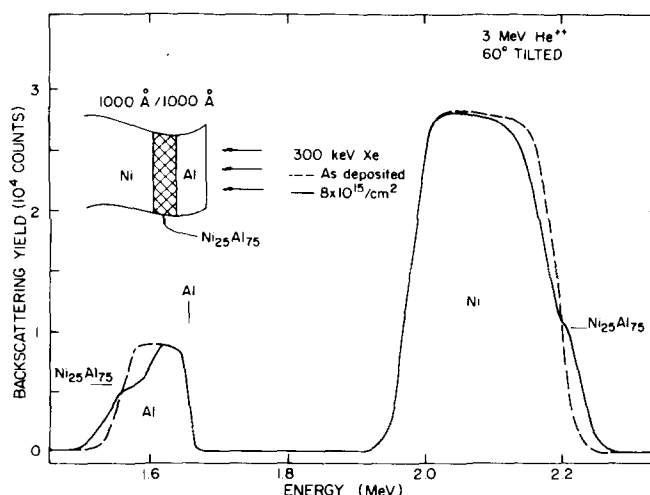


FIG. 1. Backscattering spectra of bilayered Ni/Al sample after ion beam mixing with Xe ions. The composition of the mixed layer at the Ni/Al interface is Ni<sub>25</sub>Al<sub>75</sub>.

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# Ni/Al BILAYER REACTIONS

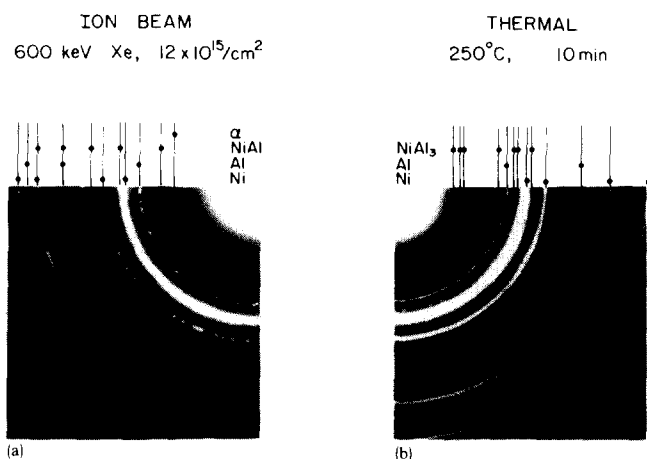


FIG. 2. Electron diffraction patterns from reacted Ni/Al bilayers. (a) Diffraction pattern from an ion mixed bilayer indicates the production of two phases, NiAl and an amorphous mixture ( $\alpha$ ). (b) Thermal reactions in the bilayer result in the formation of NiAl<sub>3</sub> after 10 min at 250 °C.

than in Ni/Al samples. For example, when Pd/Al samples were subjected to Xe irradiation at a dose of  $1 \times 10^{15}/\text{cm}^2$ , RBS spectra showed the formation of an interface alloy (Fig. 3). The atomic composition of the layer was determined from the spectra step heights to be Pd<sub>67</sub>Al<sub>33</sub>. Electron diffraction patterns taken of bilayer samples reacted with ion doses ranging from  $5 \times 10^{14}/\text{cm}^2$  to  $12 \times 10^{15}/\text{cm}^2$  revealed that the only crystalline phase formed was PdAl (Fig. 4). The formation of the compound PdAl, as determined by diffraction, was observed at the lowest mixing dose used. As the ion dose is increased, the Pd diffraction rings undergo broadening indicating the incorporation of Al into the Pd lattice. With a further increase in dose, complete attenuation of the Pd signal occurs and the presence of a diffuse ring, indicative of amorphous mixture appears. In addition to the diffuse ring, diffraction patterns from PdAl and Al are still ob-

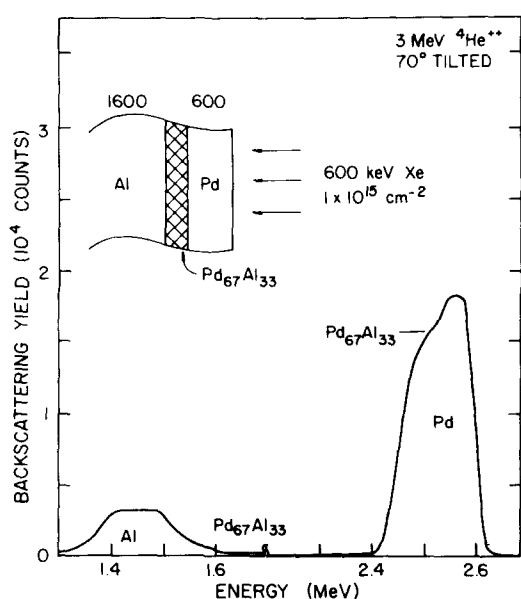


FIG. 3. Backscattering spectra from an ion reacted Pd/Al bilayer. Steps in the spectra indicate an interface mixture with composition Pd<sub>67</sub>Al<sub>33</sub>.

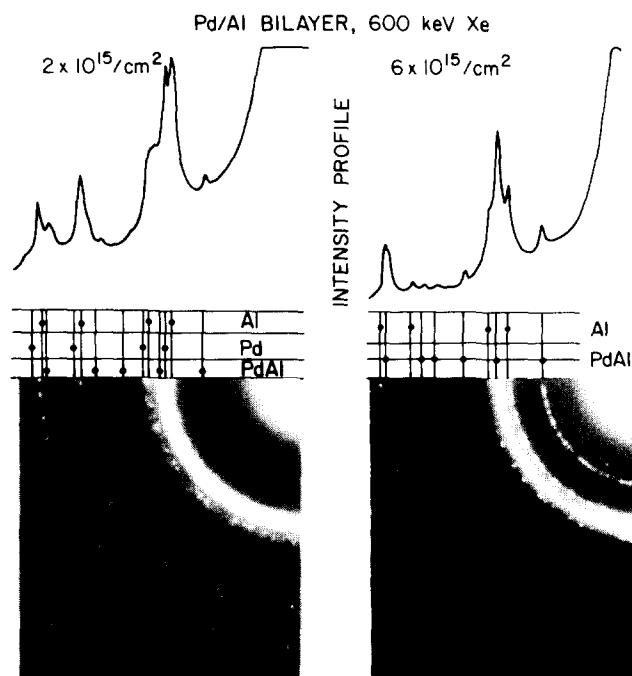


FIG. 4. Electron diffraction patterns from ion mixed Pd/Al bilayers. Diffraction rings from samples implanted with  $2 \times 10^{15}$  Xe ions/ $\text{cm}^2$  (left) indicate the presence of Pd, Al, and the compound PdAl. At higher doses (right), complete attenuation of the Pd signal occurs along with an enhancement in the PdAl signal.

served. No other compounds were identified by diffraction during the mixing process.

Diffraction measurements made during *in situ* annealing indicated that the first compound which formed thermally was PdAl<sub>4</sub>. This intermetallic was observed after 10 min at 200 °C. Further annealing at this temperature resulted in the coexistence of both PdAl<sub>4</sub> and PdAl<sub>3</sub>. These thermal compounds differ from the ion mixed crystalline compound PdAl. Previous thermal studies of thin-film reactions in Pd/Al bilayers are in disagreement with our finding of PdAl<sub>4</sub> as the first phase. Some investigators have identified PdAl<sub>3</sub> as the first intermetallic,<sup>6</sup> while others found PdAl.<sup>7</sup>

Backscattering spectra taken from ion mixed Pt/Al bilayers showed signs of step evolution as early in dose as  $2.5 \times 10^{14}$  Xe ions/ $\text{cm}^2$ . Electron diffraction examination of mixed bilayers revealed the presence of two diffuse bands in addition to signals from Pt and Al in the diffraction pattern. As the dose was increased the intensity of the diffuse band was also found to increase while the Pt diffraction intensity decreased. Further increases in dose resulted in the total attenuation of the Pt signal and only diffraction from Al and an amorphous phase was observed. This condition persists up to the final dose of  $12 \times 10^{15}$  Xe ions/ $\text{cm}^2$ . At no time during the mixing process did electron diffraction reveal the presence of any crystalline intermetallic compound.

Diffraction patterns taken during the thermal reaction of as-deposited Pt/Al bilayers revealed that the first thermal intermetallic to form was Pt<sub>2</sub>Al<sub>3</sub>. This compound could be identified after a 15-min anneal at 300 °C. The formation of Pt<sub>2</sub>Al<sub>3</sub> as the first phase after thermally reacting Pt/Al bilayers has been observed previously.<sup>8</sup>

A summary of the ion beam and thermal reactions ob-

TABLE I. Bilayer thermal and ion beam reactions.

System	First thermal phase (TEM)	First ion mixed composition (RBS)	First ion mixed crystalline phase (TEM)
Pt/Al	Pt <sub>2</sub> Al <sub>3</sub>	Pt <sub>40</sub> Al <sub>60</sub>	$\alpha$
Ni/Al	NiAl <sub>3</sub>	Ni <sub>25</sub> Al <sub>75</sub>	NiAl
Pd/Al	PdAl <sub>4</sub>	Pd <sub>67</sub> Al <sub>33</sub>	PdAl

tained in this study is presented in Table I. These results differ from those with ion mixing Si/metal bilayers. For silicides the first thermal phases and the first ion mixed composition have the same atomic composition. In addition, the composition of the ion induced crystalline phase and interface mixture are also the same for a majority of the silicide systems studied.<sup>4</sup> In comparison we see from the data in Table I that for Al/metal bilayers the first thermal intermetallic compounds produced were Pt<sub>2</sub>Al<sub>3</sub>, NiAl<sub>3</sub>, and PdAl<sub>4</sub>. In contrast, ion induced reactions resulted in the production of an amorphous mixture between Pt and Al while the crystalline compounds NiAl and PdAl were formed when Ni/Al and Pd/Al bilayers were mixed. The atomic compositions of the ion mixed layer differ from the composition of the irradiation induced crystalline compound. The ion mixed layer compositions were found to be Pt<sub>40</sub>Al<sub>60</sub>, Ni<sub>25</sub>Al<sub>75</sub>, and Pd<sub>67</sub>Al<sub>33</sub> while the ion induced crystalline compound compositions were Ni<sub>50</sub>Al<sub>50</sub> and Pd<sub>50</sub>Al<sub>50</sub>. Since no crystalline compounds were observed after the ion mixing of Pt/Al bilayers no composition comparisons can be made. It is obvious from these results that RBS observations by themselves are not sufficient for determining what compounds or phases are truly present in the ion reacted samples.

It should be noted that the crystalline compounds produced by the ion mixing of Pd/Al and Ni/Al bilayers, PdAl and NiAl, both possess the same cesium chloride structure. This structure is a primitive cubic with two atoms per unit cell. The remaining equilibrium compounds that can exist in the three bimetallic systems studied all possess structures of greater complexity. It has previously been suggested that the radiation hardness of a crystalline compound is dependent on the structure of that compound. The structure of com-

pounds observed to have a maximum of insensitivity to Xe irradiation has been of the cesium chloride type, while other more complex structured compounds have been rendered amorphous after irradiation.<sup>9</sup>

The fact that compositions do result from the ion mixing of Al/metal bilayers suggests that chemical driving forces are in operation along with ballistic mixing during the irradiation process. The observation that the crystalline compounds formed by ion mixing differ from the ion mixed composition indicates that crystal compound formation in the cascade is dependent on nucleation and growth kinetics. Thus, even when ion mixed interface compositions are favorable for the formation of a particular compound, actual crystalline compound formation is limited by the high quench rate, nonequilibrium character of the cascade.

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