# Comparative study on phase formation in Al–Pd thin film by ion beam mixing and thermal annealing

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Ion beam mixing and/or thermal annealing were conducted to study the phase formation and dissociation in Al–Pd thin films. The films were prepared by sequential evaporation, $Ar^+$ ion mixed, annealed at 350 °C for 1 h under vacuum and then analysed by RBS, TEM and XPS. The intermetallic compounds formed by ion mixing alone are found to be $Al_3Pd_2$ and AlPd at a dose of $1.5 \times 10^{16}$ $Ar^+$ $cm^{-2}$. Thermal annealing after this radiation gave two new phases of $Al_3Pd$ and $Al_3Pd_5$ in addition to $Al_3Pd_2$ and AlPd. For an as-annealed sample without $Ar^+$ bombardment, the observed phases are $Al_3Pd$, $Al_3Pd_2$ and AlPd. The different behaviours in phase formation between ion beam mixing and thermal annealing are presented.

## 1. Introduction

Aluminium and its alloys are used extensively for metallization in integrated circuits. When aluminium is incorporated into an Al–Si shallow junction, palladium silicide has been found to be an effective barrier layer for reducing junction problems such as spiking and electromigration [1]. The Al–$Pd_2$Si–Si junction still exhibits thermal instability upon annealing above 300 °C [2]. For this reason the interaction between aluminium and palladium is important. There have been a number of investigations about the interdiffusion and intermetallic phase formation between aluminium and palladium with thermal annealing. There have been several disagreements between investigations on the phase formation and dissociation [3–6].

Although an ever-increasing interest exists in the utilization of ion beams to induce the intermetallic compound formation by ion beam mixing (IBM), very few studies [6] have been done by IBM in Al–Pd thin films which contradict with thermal annealing. Recently, we investigated the basic mechanisms involved in the IBM process on the Al–Pd system where we found that the diffusivity for aluminium is larger than that of palladium by two orders of magnitude [7].

In addition the IBM process is known to be an effective method for the formation of equilibrium or metastable compounds [8], there is also some basic interest in studying the phase stability upon further processing at a higher temperature. In connection with this the object of this paper is to investigate the phase formation and decomposition with IBM and/or thermal annealing in Al–Pd thin films.

## 2. Experimental procedures

Bimetallic films of aluminium and palladium were sequentially deposited on the slide glass by electron beam evaporation in a vacuum of about $10^{-7}$ torr. The samples were then irradiated with $Ar^+$ ions to induce the mixing. Ion beam mixing was carried out at a pressure of $2 \times 10^{-7}$ torr at room temperature. The aluminium thicknesses of 50 and 30 nm were chosen so as to match the maximum nuclear stopping power with the Al–Pd interfaces using the TRIM code for 78 and 40 keV $Ar^+$ ion, respectively. Doses from $5 \times 10^{15}$ to $1.5 \times 10^{16}$ $cm^{-2}$ were used for mixing the bilayers of Al–Pd with an average beam current density of 0.5 $\mu A$ $cm^{-2}$. The thin-film interactions were analysed with Rutherford backscattering spectrometry (RBS). Samples for transmission electron microscopy (TEM) studies were deposited onto a freshly cleaved NaCl substrate which was later dissolved away in de-ionized water and they were then floated onto copper grids. Some of the Al–Pd layers were annealed at 350 °C for 1 h in quartz tube evacuated to less than $10^{-6}$ torr. The AlK$\alpha$ line is used as an X-ray source for X-ray electron spectroscopy (XPS).

## 3. Results and discussions

Fig. 1 shows the RBS spectrum of Al(50 nm)–Pd(20 nm)–glass before and after ion beam mixing (IBM) with 78 keV $Ar^+$ at room temperature. The correct yield for $Al_3Pd_2$ and AlPd phases are marked for the surface of palladium signal. The spectra show that the induced phase by IBM is found to be the mixture of $Al_3Pd_2$ and AlPd intermetallic compound

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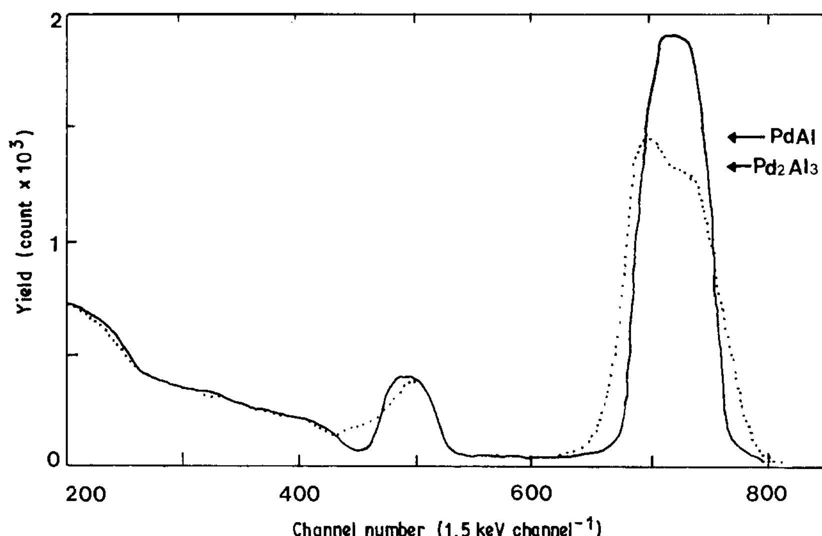


*Figure 1* RBS spectra showing the formation of $Al_3Pd_2$ and AlPd compounds after irradiation with $1 \times 10^{16}\ Ar^+\ cm^{-2}$ on Al(50 nm)–Pd(20 nm). The unirradiated sample is included for comparison. (—— as-deposited, ...... $1 \times 10^{16}\ Ar^+\ cm^2$)

at a dose of $1 \times 10^{16}\ Ar^+\ cm^{-2}$. It is not, however, clear from this figure which one is the initial phase formed by IBM.

To make clear this point, a selected area diffraction (SAD) with TEM was employed on a sample having irradiated with $5 \times 10^{15}\ Ar^+\ cm^{-2}$. As shown in Fig. 2a the phase present was determined to be $Al_3Pd_2$, and the unreacted polycrystalline palladium and aluminium remained after this dose of irradiation. At a higher dose of $1 \times 10^{16}\ Ar^+\ cm^{-2}$ AlPd phase was appeared in addition to $Al_3Pd_2$ as shown in Fig. 2b. At this dose the palladium totally disappeared but the aluminium still remained due to its initial layer (50 nm) being thicker than that of palladium (20 nm). With a further bombardment with $1.5 \times 10^{16}\ Ar^+\ cm^{-2}$ $Al_3Pd_2$ phase begins to disappear judged by the intensity of SAD pattern, but still be found as shown in Fig. 2c. Recently Hung *et al.* [9] found that AlPd is insensitive to ion bombardment and remains crystalline, and they further reported that the decomposition of $Al_3Pd_2$ to AlPd and an amorphous phase occurs with $Xe^+$ irradiation. Their results are in good agreement with the present experiment except that no amorphous phase is found in our sample due to the different ion ($Ar^+$) being used here. This indicates that the phase formation and dissociation highly depend upon the mass of ion employed in IBM.

Recently Colgan [3] reported that the initial phase formed by thermal annealing was $Al_3Pd_2$ which is similar to the present experiment. The disagreements between investigators on the initial phase in Al–Pd system have been reported. Köster *et al.* [4] found that the initial phase formed by thermal reaction was AlPd, which was followed by $Al_3Pd_2$. Howard *et al.* [5] also reported that $Al_3Pd$ was the initial phase and it grew between 250 and 350 °C. Work by Nastasi *et al.* [6] found $Al_4Pd$ as the initial phase during *in situ* annealing, but they claimed that the first ion mixed phase confirmed by TEM was AlPd which differs from this present experiment.

The Al–Pd phase diagram has not yet been determined with precision [10]. Although the existence of nine equilibrium intermediate phases appears to be reliably established, the diffraction standard (JCPDS) is not well characterized except for a few compounds. The incomplete diffraction standards and the very similar lattice spacings between these intermediate phases make the identification of phases present very complicated except for a few cases, which might lead to disagreement between investigators. Another technology other than TEM and RBS, such as X-ray photoelectron spectroscopy (XPS) with surface sensitive capability for the chemical information, should, therefore, be employed for the determination of the phases involved.

A XPS valance band (VB) spectrum on Pd(5 nm)–Al(15 nm)–glass is shown in Fig. 3. A consecutive XPS spectrum of palladium valance band (VB) during *in situ* annealing are taken. As can be seen in this figure, the binding energy of 1.8 eV for as-deposited sample shifts to 4.8 eV after heat treatment at 200 °C for 5 min. This chemical shift observed at above 200 °C

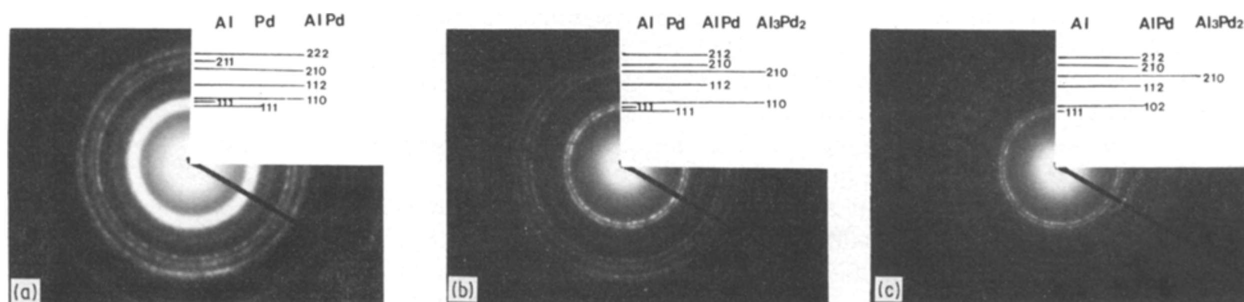


*Figure 2* TEM diffraction patterns for (a) $5 \times 10^{15}\ Ar^+\ cm^{-2}$, (b) $1 \times 10^{16}\ Ar^+\ cm^{-2}$, (c) $1.5 \times 10^{16}\ Ar^+\ cm^{-2}$ irradiated Al(50 nm)–Pd(20 nm).

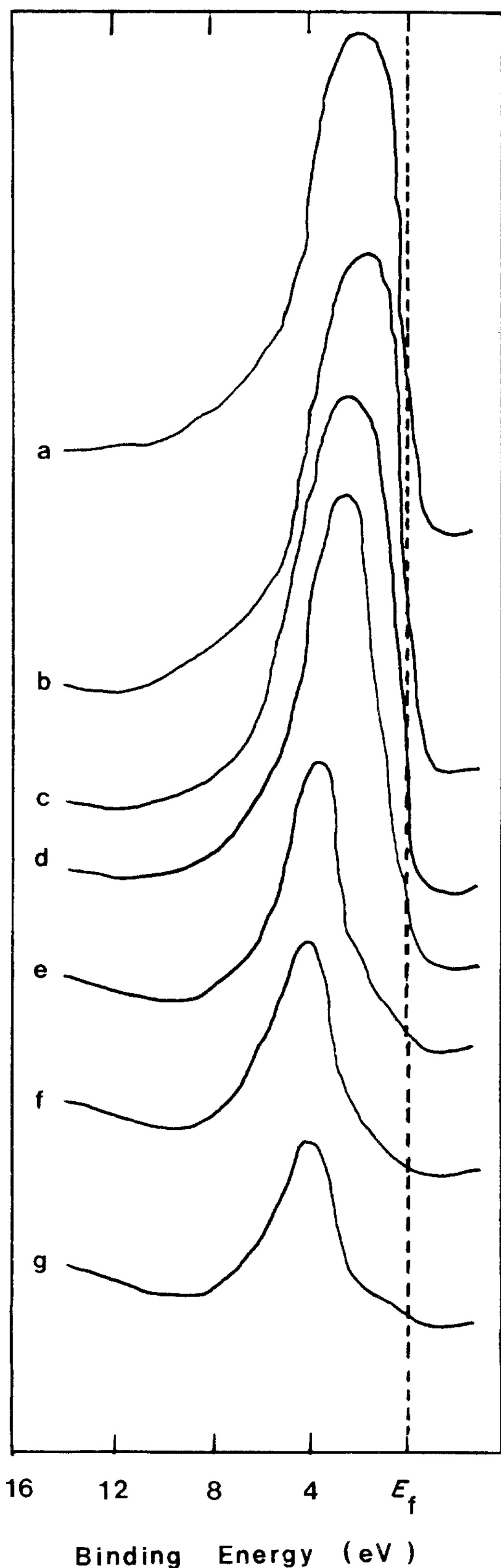


*Figure 3* Consecutive XPS valence band spectrum of palladium for Pd(5 nm)–Al(15 nm) with *in situ* thermal annealing. (a) as-deposited, (b) 150 °C for 5 min, (c) 200 °C for 5 min, (d) 200 °C for 10 min, (e) 200 °C for 15 min, (f) 250 °C for 5 min, (g) 300 °C for 5 min.

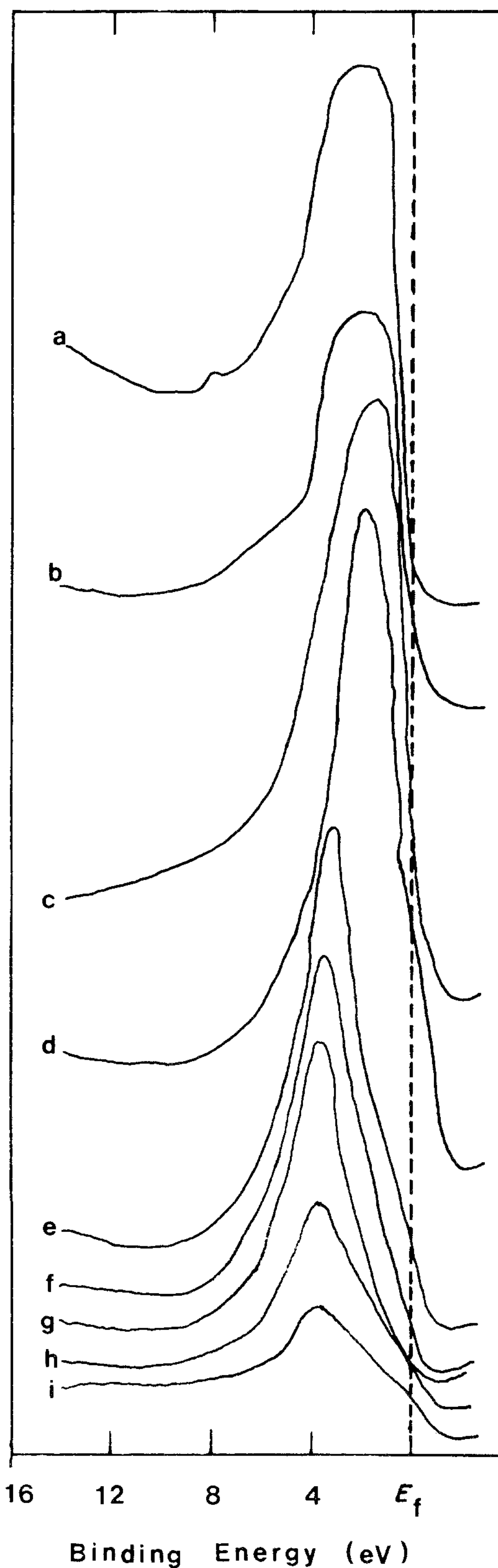


*Figure 4* XPS spectrum with sputtering for irradiated sample Pd(5 nm)–Al(15 nm) with dose $1 \times 10^{16}$ $Ar^+$ $cm^{-2}$ at 78 keV. (a) 2 min, (b) 7 min, (c) 17 min, (d) 36 min, (e) 46 min, (f) 56 min, (g) 66 min, (h) 86 min, (i) 106 min sputtering.

indicates that the compound $Al_xPd_{1-x}$ is formed at these temperatures. The previously published XPS data show [11] that the binding energies are 4.8 and 3.6 eV for $Al_3Pd$ and AlPd, respectively. It can be easily concluded, therefore, that the initial phase formed by thermal reaction in the Al–Pd system is to be $Al_3Pd$ which again coincides with Howard *et al.* [5].

XPS spectra were also taken on ion beam mixed samples with a dose of $1 \times 10^{16}$ $Ar^+$ $cm^{-2}$ at 78 keV. Fig. 4 shows the XPS spectrum on this sample with sputtering. The binding energy of around 1 eV before sputtering shifts to 4.0 eV after sputtering for 106 min. This shifted binding energy of 4.0 eV for ion beam mixed specimen differs with the chemical shift of

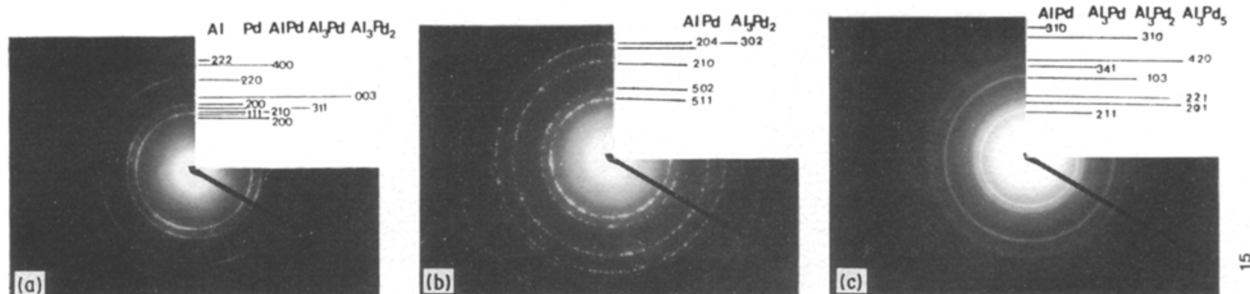


*Figure 5* TEM diffraction patterns for ion mixed followed by thermal annealing at 350 °C for 1 h in vacuum. (a) as-deposited without $Ar^+$ ion bombardment, (b) $5 \times 10^{15}$ $Ar^+$ $cm^{-2}$, (c) $1.5 \times 10^{16}$ $Ar^+$ $cm^{-2}$ ion mixed with 40 keV prior to thermal annealing Al(30 nm)–Pd(50 nm).

4.6 eV for heat-treated ones. The observed 4.0 eV binding energy is thought to be possibly associated with the formation of AlPd (BE = 3.6 eV) and $Al_3Pd_2$ (BE is not known) which is coincident with the results of TEM and RBS as discussed before. As can be seen the shift in BE is increased slowly with sputtering. If the sputtering was done beyond 106 min to reach the interface between aluminium and palladium it is highly anticipated, although it is not confirmed in this experiment, that the binding energy of 4.6 eV corresponding to $Al_3Pd$ might to be appeared in ion beam mixed samples as found in heat treated one as described before. In connection with this, further work is required to check that initial phase formed by IBM is the same as that obtained by thermal annealing.

In order to study phase transitions further for the irradiated samples after thermal annealing, Al(30 nm)–Pd(50 nm)–NaCl samples were initially irradiated with 40 keV $Ar^+$ ions at room temperature and then thermal annealed at 350 °C for 1 h in a vacuum furnace. For an as-annealed sample without $Ar^+$ bombardment, the observed phases are $Al_3Pd$, $Al_3Pd_2$, AlPd, aluminium and palladium as shown in Fig. 5a. It is interesting to note that unreacted aluminium and palladium still remained after heat treatment at 350 °C. The irradiated sample with a dose $5 \times 10^{15}$ $Ar^+$ $cm^{-2}$ and then heat-treated gives $Al_3Pd_2$ and AlPd phases (Fig. 5b). Compared to Fig. 5a, the palladium and aluminium were totally consumed to produce the compounds after irradiation and heat-treatment. This increased reaction rate between aluminium and palladium by ion beam prior to thermal annealing arises due to the radiation enhanced diffusion (RED) associated with the defect generation during ion bombardment [12]. The phase of $Al_3Pd$ presented in Fig. 5a also disappeared in Fig. 5b with a prior $Ar^+$ bombardment before annealing, which indicates that $Al_3Pd$ is sensitive to ion bombardment or the less stable phase $Al_3Pd$ (heat of formation 1300 cal $cm^{-3}$ [3] is easily transformed into the more stable phase $Al_3Pd_2$ (heat of formation 2000 cal $cm^{-3}$) associated with the defects production by a prior ion bombardment. Recalling that the induced phase by IBM alone at room temperature with this dose of $5 \times 10^{15}$ $Ar^+$ $cm^{-2}$ is $Al_3Pd_2$ (Fig. 2a), the new phase AlPd is formed for the heat-treated sample after ion bombardment in addition to $Al_3Pd_2$ (Fig. 5b). Considering that heats of formation [3] are 2800 and 2000 cal $cm^{-3}$ for AlPd and $Al_3Pd_2$, respectively, one sees that the thermodynamically preferred phase form with thermal annealing after ion bombardment. Upon a further ion bombardment with $1.5 \times 10^{16}$ $Ar^+$ $cm^{-2}$ the phases identified, after thermal annealing, are $Al_3Pd$ and $Al_3Pd_5$ in addition to $Al_3Pd_2$ and AlPd (Fig. 5c). Compared with $Al_3Pd_2$ and AlPd phases formed by IBM alone (Fig. 2c), thermal annealing after irradiation gives two additional phases of $Al_3Pd$ and $Al_3Pd_5$. The high densities of defects which remained after IBM provide high atomic mobilities at relatively low annealing temperature of 350 °C that results in these additional new phases. From the phase diagram $Al_3Pd_5$ is stable above 615 °C. It is interesting to mention that a metastable $Al_3Pd_5$ intermetallic compound is formed with a relatively low temperature annealing of 350 °C after IBM. There are many reports [8] that metastable phases are formed with IBM due to the non-equilibrium nature of this process.

For metal–metal systems, it is known [8] that the first phase formed by ion mixing is not always the same as that obtained by thermal annealing. From this experiment we found that the behaviour of phase formation or dissociation also differs in the two cases. It has been proposed that selective phase growth is mainly due to the interfacial composition, which is determined by the supply of atoms to the interface [13]. Since the defects produced during ion beam mixing affect the atomic mobilities and also the interfacial composition changes with irradiation [7], the different behaviour of phase formation between IBM and thermal annealing process is easily understood.

## 4. Conclusions

Ion beam mixing and/or thermal annealing were conducted to study the phase formation and dissociation in Al–Pd thin films. RBS spectra show that intermetallic compounds of $Al_3Pd_2$ and AlPd are formed with $1 \times 10^{16}$ $Ar^+$ $cm^{-2}$ irradiation at room temperature. TEM analysis shows that $Al_3Pd_2$ is formed with IBM at room temperature with dose of $5 \times 10^{16}$ $Ar^+$ $cm^{-2}$. At a higher dose of $1 \times 10^{16}$ $Ar^+$ $cm^{-2}$ the AlPd phase appear in addition to $Al_3Pd_2$ and unreacted aluminium.

XPS analysis shows that the binding energy of 1.8 eV of the palladium valence band for the as-deposited sample shifts to 4.8 eV after thermal annealing at 200 °C for 5 min, which implies the formation of initial compound $Al_3Pd$. For the irradiated sample with a dose $1.5 \times 10^{16}$ $Ar^+$ $cm^{-2}$ and then

heat-treated at 350 °C for 1 h, $Al_3Pd$, $Al_3Pd_2$, AlPd and metastable $Al_3Pd_5$ are formed. No unreacted aluminium and palladium remained after these treatments compared with the as-annealed one.

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