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Stability of Ir–Ta Diffusion Barriers

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Abstract

The thermal and chemical stability of amorphous and crystalline Ir–Ta diffusion barriers between silicon and aluminium is investigated. A failure temperature of 550 °C is found for amorphous $Ir_{45}Ta_{55}$ at the aluminium interface. The reaction between amorphous $Ir_{45}Ta_{55}$ and silicon occurs at temperatures as high as 875 °C. The latter reaction temperature is lowered to 700 °C when crystalline Ir–Ta is used.

1. Introduction

Miniaturization in very-large-scale integrated (VLSI) electronics requires complex multilevel structures whose stability strongly depends on interdiffusion and reaction of adjoining layers. Thin film diffusion barriers are needed to form stable layers, especially in the presence of aluminium (applied as a low resistivity contact or interconnect) which has a low reaction temperature with silicon [1, 2]. Below the Tammann temperature, which is one-half to two-thirds of the melting point of a solid (in degrees kelvin), atomic diffusion may be dominated by diffusion via defects, *e.g.* grain boundaries or dislocations, rather than bulk processes [3, 4]. Amorphous diffusion barriers are suitable to overcome this type of failure mechanism because of the absence of grain boundaries. In fact, several amorphous alloys were tested recently for their stability in contact with silicon substrates and aluminium overlayers [5–13].

In general, if an amorphous alloy consisting of a near-noble and a refractory metal exhibits a sufficiently high crystallization temperature, the alloy reacts with silicon at the temperature at which the refractory component becomes mobile. At lower temperatures the near-noble constituent is locked in the amorphous matrix and is unable to react. At higher temperatures silicon becomes sufficiently mobile to react with the near-noble and refractory constituents simultaneously. This higher temperature behaviour is typically at 600–650 °C. The reaction between aluminium and amorphous alloys occurs via the same mechanism but at approximately 450 °C.

In this paper we report on the stability of amorphous Ir–Ta in contact with silicon and aluminium. The Ir–Ta system was chosen because of its high crystallization temperature of 900 °C in free-standing thin film form [14, 15] and its high negative heat formation (of the order of −40 kJ $mole^{-1}$ [16]) indicate a high chemical stability. It has been shown by Hunt *et al.* [17] that sputter-deposited amorphous $Ir_{55}Ta_{45}$ on silicon reacts with silicon at temperatures between 850 and 900 °C, although the alloy was observed to crystallize at 760 °C. It has also been shown [18] that in an oxygen ambient amorphous Ir–Ta does not react with silicon upon heating to 900 °C. Furthermore, an amorphous $Ir_{42}Ta_{58}$ diffusion barrier 2000 Å thick between gold and silicon, annealed at 600 °C for 24 h in air, was found to be stable, with only a slight interfacial reaction with the silicon substrate [19]. These results encouraged us to perform a more complete study of amorphous Ir–Ta diffusion barriers in order to investigate interfacial reactions between amor-

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phous Ir–Ta and silicon as well as aluminium. For comparison we performed experiments with crystalline Ir–Ta alloys also.

2. Experimental details

Amorphous $Ir_{45}Ta_{55}$ alloys were deposited to a thickness of 350 Å in a dual-electron-gun evaporator with a base pressure of less than 1×10^{-6} Pa. At a typical deposition rate of 2 Å s^{-1} the pressure during deposition was less than 1×10^{-5} Pa. The composition of the alloys was monitored during deposition using a quadrupole mass spectrometer. The thickness of the deposited films was measured *in situ* with a quartz crystal monitor. The substrates ((100) Si, Si_3N_4 and NaCl) were kept at liquid nitrogen temperature during deposition. Also, 500 Å of aluminium was evaporated on top of part of the samples. Annealing was carried out in a vacuum furnace at a background pressure of less than 2×10^{-5} Pa. Compositional depth profiles were measured with 2 MeV He^+ Rutherford-backscattering spectrometry (RBS). The phase identification was done with X-ray diffraction (XRD) using a conventional powder diffractometer. Transmission electron microscopy (TEM) analysis was done on the 125 Å thick amorphous $Ir_{45}Ta_{55}$ samples evaporated onto NaCl substrates. Further, 350 Å of silicon was deposited on part of these samples and 250 Å of aluminium was deposited on the other part. Before annealing, the NaCl substrates were dissolved in deionized water and the films were mounted on molybdenum TEM grids. Also, a crystalline $Ir_{75}Ta_{25}$ alloy was deposited onto Si_3N_4 and NaCl substrates to thicknesses of 350 and 125 Å respectively. A layer of amorphous silicon (1000 and 350 Å respectively) was then deposited on top of these structures in order to study the influence of Ir–Ta crystallinity on the reaction with silicon. The chosen composition is just outside the glass-forming range [15]. To insure deposition of crystalline phases, the Si_3N_4 substrates were heated to 400 °C during deposition of the $Ir_{75}Ta_{25}$ alloy.

3. Results

In agreement with data from the literature [14, 15], crystallization of thin film amorphous $Ir_{45}Ta_{55}$ (a-$Ir_{45}Ta_{55}$) occurred at 900 °C by phase separation into β-Ta and iridium. This was observed with TEM for self-supporting films as well as with XRD for the films deposited onto Si_3N_4 substrates.

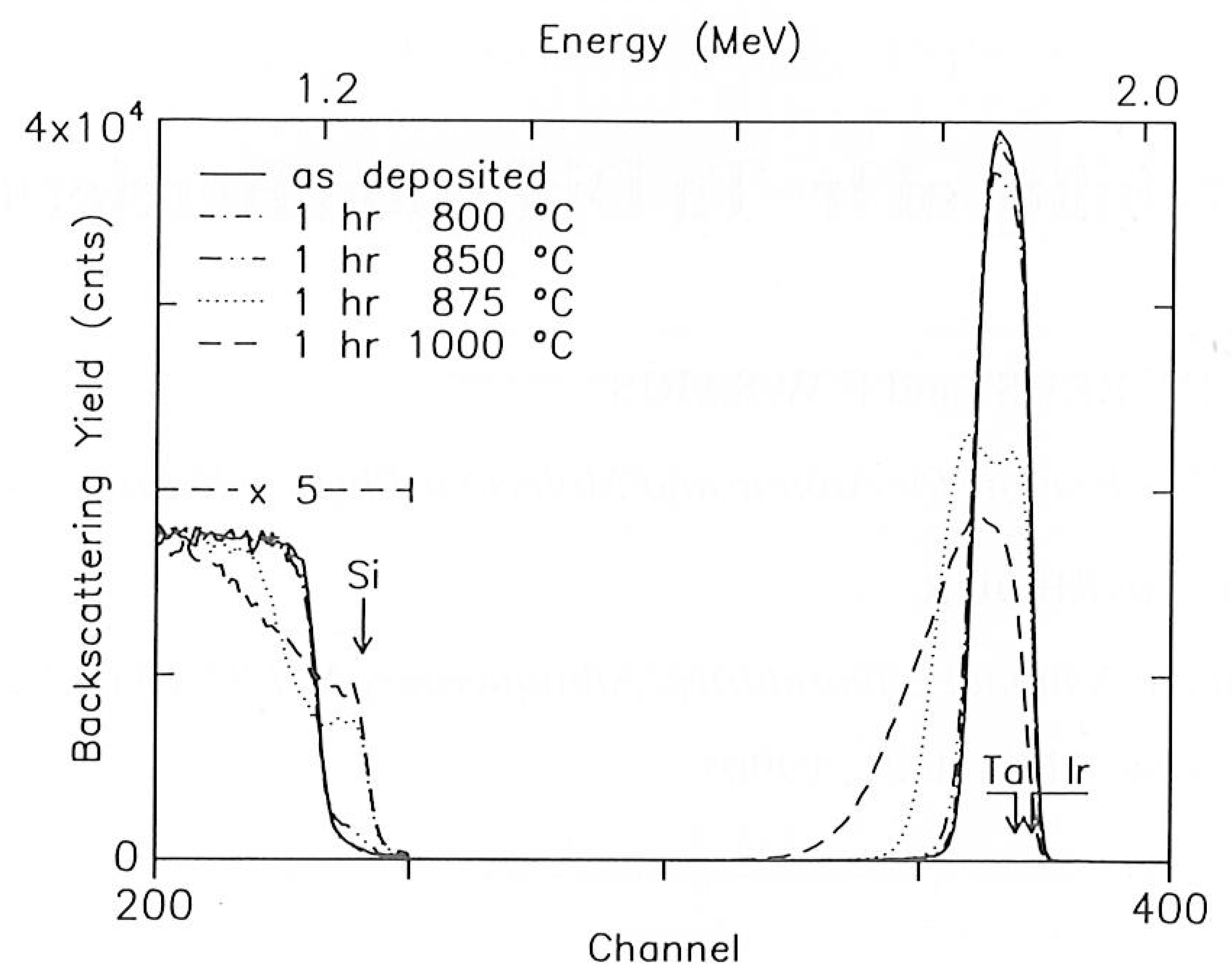

Fig. 1. 2 MeV $^4He^+$ RBS spectra of (100) Si–a-$Ir_{45}Ta_{55}$ samples before and after reacting. Sample tilt 7°, scattering angle 130°. Surface channels are indicated by arrows.

Figure 1 shows RBS spectra after annealing of the Si–a-$Ir_{45}Ta_{55}$ samples. The surface peak positions for silicon, tantalum and iridium are indicated by arrows. The iridium and tantalum signals appear at the surface peak position in the spectrum of the as-deposited sample (solid line). However, the separate iridium and tantalum peaks cannot be distinguished in RBS because the heavy masses of iridium and tantalum are very close. The silicon signal is found below the surface peak position. The steep silicon edge and Ir–Ta trailing edge show that the Si–a-$Ir_{45}Ta_{55}$ interface is sharp. The spectrum obtained after annealing for 1 h at 800 °C is almost identical to the spectrum of the as-deposited sample, indicating that no interdiffusion occurred. Slight changes are observed after annealing at 850 °C, and a reaction between silicon and amorphous $Ir_{45}Ta_{55}$ took place during annealing at 875 °C (dotted line). This reaction is exhibited by a broadening and a decrease in height of the Ir–Ta signal. A plateau is observed in the silicon signal and silicon is found at the sample surface, indicating complete intermixing to form a nearly uniform layer with a "sharp" silicon interface. The interface between the silicon substrate and the reacted layer is irregular after annealing for 1 h at 1000 °C, as can be seen by the slope in the silicon signal and the Ir–Ta trailing edge.

XRD (not shown) confirms that the reaction between silicon and amorphous $Ir_{45}Ta_{55}$ takes place at 875 °C. The only phases observed in samples annealed below 875 °C are amorphous

Ir–Ta and single-crystal silicon. At the reaction temperature of 875 °C polycrystalline $TaSi_2$, IrSi and some $IrSi_3$ are identified. All peaks in the XRD spectrum of a sample annealed for 1 h at 1000 °C can be assigned to $TaSi_2$ and $IrSi_3$. The same reactions are observed with TEM for the a-$Ir_{45}Ta_{55}$–a-Si samples. In fact, the initially amorphous silicon crystallizes (c-Si) between 600 and 700°C. The a-$Ir_{45}Ta_{55}$–c-Si structure formed in this way is stable for 1 h at temperatures lower than 900 °C. At 900 °C a reaction takes place, as can be seen in the TEM micrographs of Fig. 2. Approximately half of the sample exhibited a reaction and the bright field image of Fig. 2 shows the transition from the unreacted (region (a)) to the fully reacted (region (c)) regions. The diffraction pattern corresponding with the unreacted region (Fig. 2(a)) shows both a broad halo characteristic of the amorphous $Ir_{45}Ta_{55}$ phase and sharp diffraction lines arising from the poly-

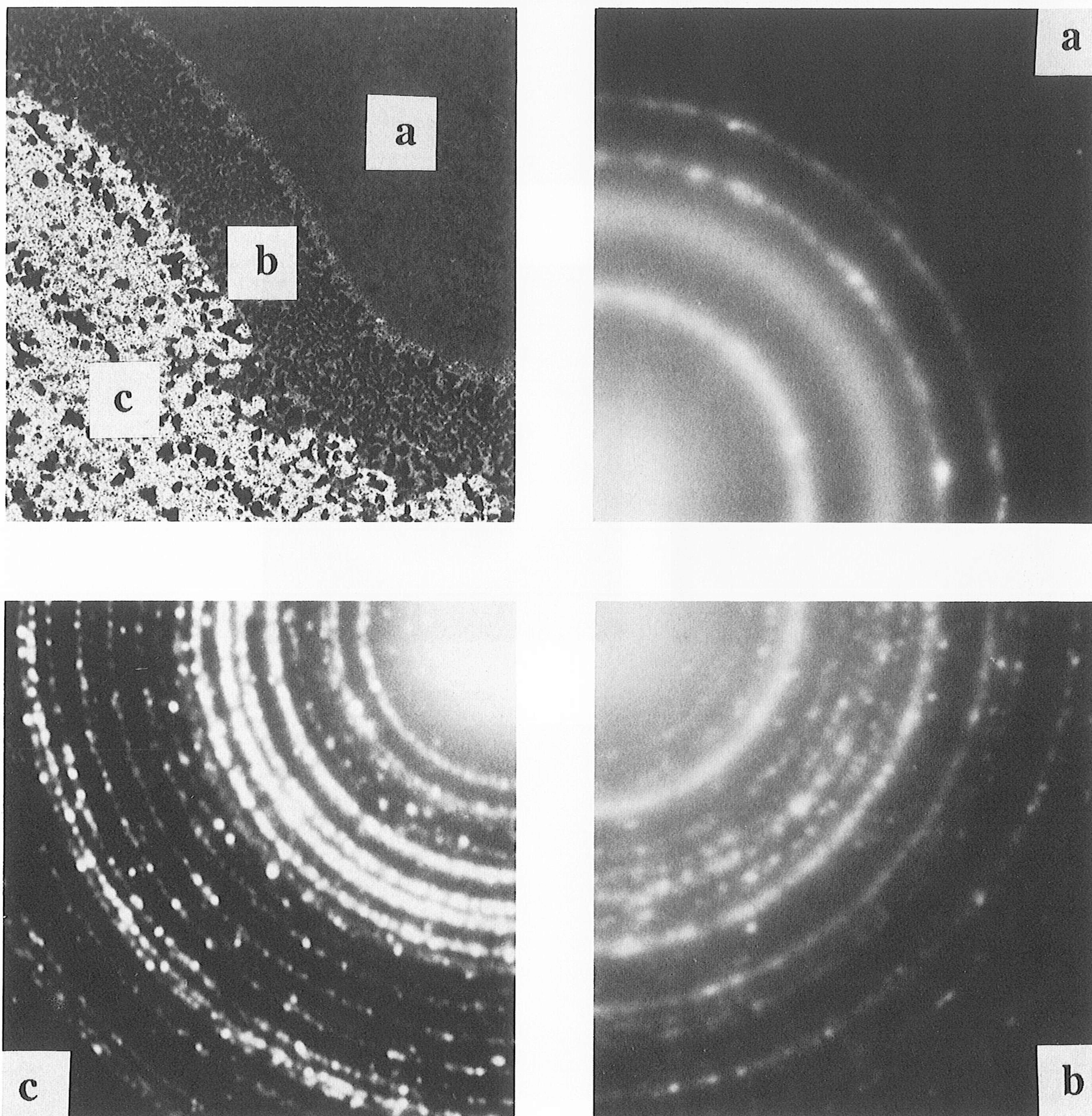

Fig. 2. TEM micrographs of a partially reacted a-$Ir_{45}Ta_{55}$–a-Si sample after annealing for 1 h at 900 °C. The bright field image shows an area of 10×10 μm^2. Region (a) and the corresponding selected area diffraction pattern show unreacted amorphous $Ir_{45}Ta_{55}$ and polycrystalline silicon. Region (b) shows the first reaction step during which $TaSi_2$ and IrSi are formed; silicon is also observed. Region (c) is characteristic for complete reaction and only $TaSi_2$ and $IrSi_3$ are observed.

crystalline silicon. The diffraction pattern of Fig. 2(b) (region (b)) shows that the amorphous phase is absent and crystalline $TaSi_2$, IrSi and silicon are observed. In region (c) the reaction has proceeded and all the silicon has been consumed to form $TaSi_2$ and $IrSi_3$ (Fig. 2(c)).

The reaction between amorphous $Ir_{45}Ta_{55}$ and aluminium can be seen in the TEM images of Fig.

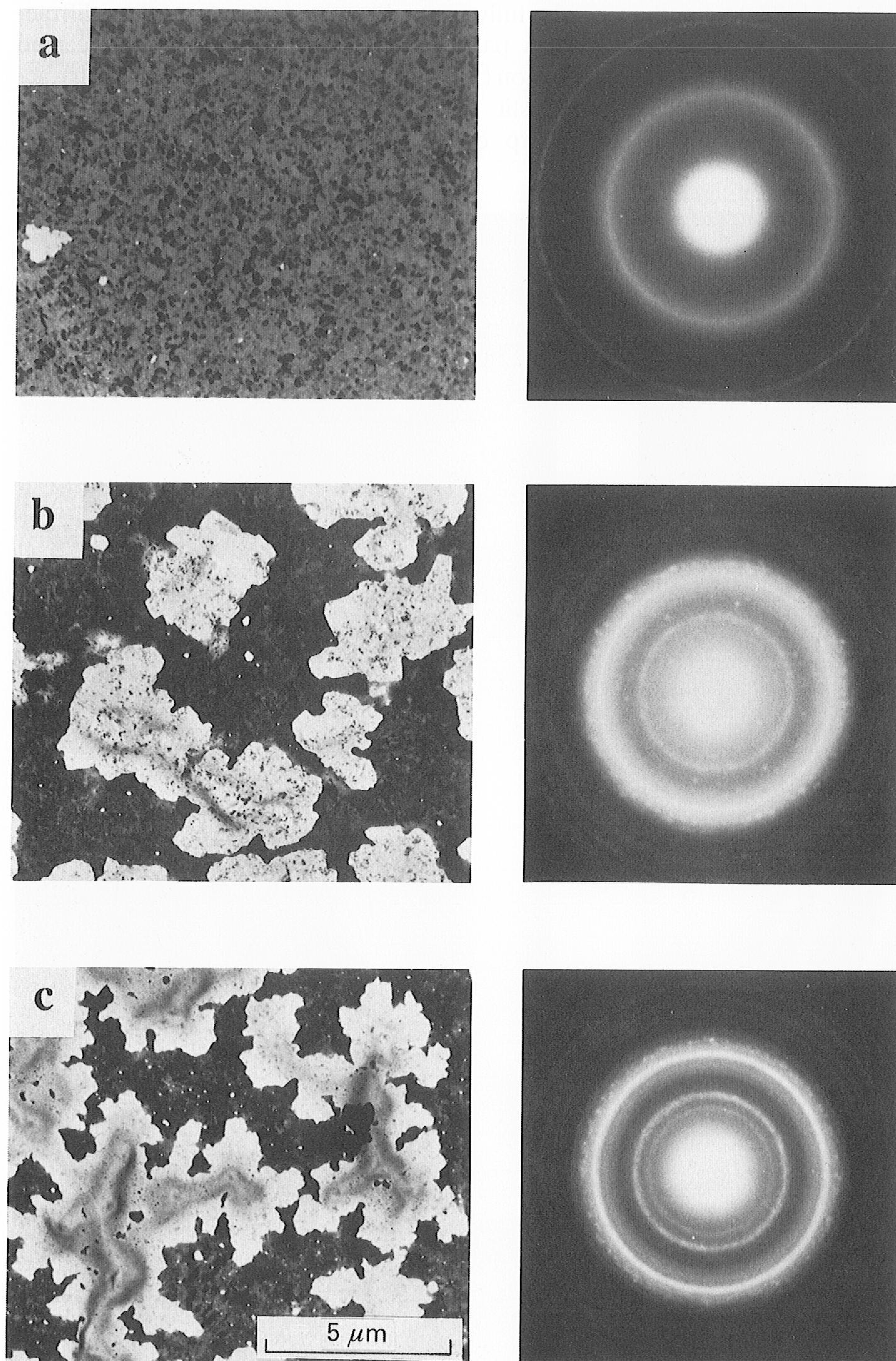

Fig. 3. TEM micrographs of a-$Ir_{45}Ta_{55}$–Al samples. (a) After annealing for 30 min at 400 °C no reaction occurred and only amorphous $Ir_{45}Ta_{55}$ and polycrystalline aluminium are observed; some pinholes have formed in the aluminium film. (b) At 550 °C Al_3Ta starts to form and the aluminium has formed islands; the selected area diffraction pattern is taken from an aluminium-covered (dark) region; the light regions are amorphous $Ir_{45}Ta_{55}$. Above 600 °C Al_3Ta and IrAl are formed. Measurement (c) is taken after annealing at 650 °C.

3. After annealing for 30 min at 400 °C (Fig. 3(a)), amorphous Ir–Ta and crystalline aluminium are the only phases observed; yet some pinholes begin to form in the aluminium, as can be seen in the bright field image. At higher anneal temperatures the aluminium starts to form islands as shown in Fig. 3(b) which is obtained from a sample annealed at 550 °C. The light regions are pure amorphous Ir–Ta whereas the dark regions contain both Ir–Ta and aluminium. Changes in the diffraction pattern also confirm that the reaction begins at this temperature. The reaction product is identified as Al_3Ta. Above 600 °C amorphous Ir–Ta reacts with aluminium to form Al_3Ta as well as IrAl, as demonstrated in the diffraction pattern of Fig. 3(c) which is taken from a sample annealed for 30 min at 650 °C.

The RBS spectra of the Si-a-$Ir_{45}Ta_{55}$–Al samples are depicted in Fig. 4. The spectrum of the as-deposited sample (solid line) shows that aluminium is found at the surface peak position, which is indicated with an arrow. A well-defined Ir–Ta signal is found below the surface peak position and the silicon signal can be observed at lower energies. The silicon peak is separated from the aluminium signal owing to the intermediate Ir–Ta layer. Aluminium islanding, inferred from the TEM results above, is noticed best in the RBS spectra by the appearance of the Ir–Ta signal at the surface peak position for samples annealed at 400 °C. However, the slopes and positions of the silicon signal and the Ir–Ta trailing edge remain unchanged, indicating that no reaction or interdiffusion occurred at the substrate interface. Similar spectra are observed after annealing at 550, 600 and 650 °C, although the Ir–Ta surface peak has significantly increased.

The influence of the amorphicity on the reaction with silicon was studied with the same type of experiments but using a crystalline $Ir_{75}Ta_{25}$ alloy instead of amorphous $Ir_{45}Ta_{55}$. Reactions in the Si_3N_4-c-$Ir_{75}Ta_{25}$–Si sample structures can be seen in Fig. 5, where results of RBS measurements are plotted. The spectrum of the as-deposited sample (solid line) shows that the silicon top layer appears at the silicon surface peak position and is separated from the silicon in the substrate, which can be found at lower energies. The Ir-Ta peak is well defined and shifted towards lower energies with respect to the iridium and tantalum surface peak positions. After annealing at 650 °C, slight changes in the spectrum indicate the onset of a reaction which

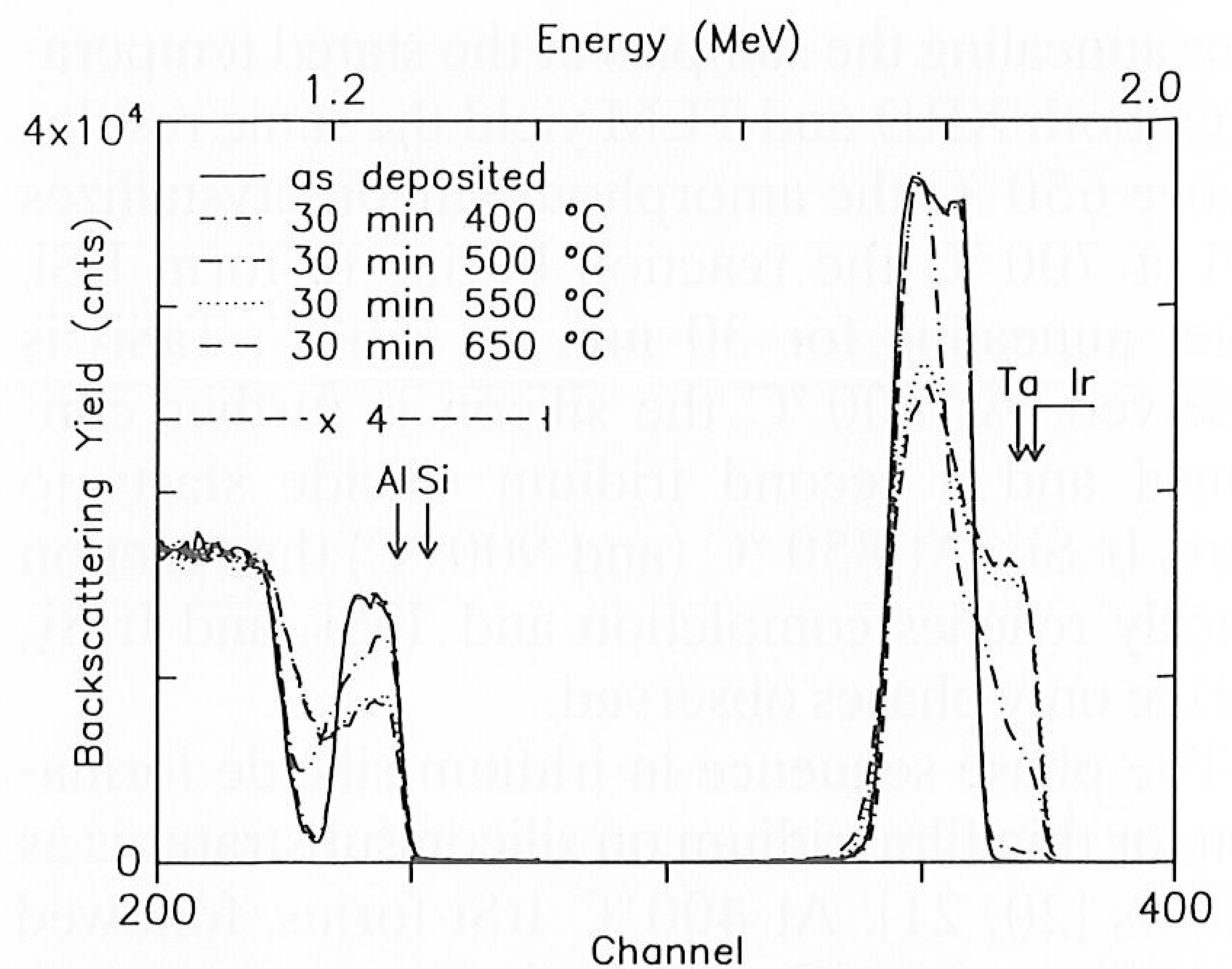

Fig. 4. 2 MeV $^4He^+$ RBS spectra of Si-a-$Ir_{45}Ta_{55}$–Al samples. Sample tilt 7°, scattering angle 125°. At 400 °C and higher temperatures aluminium starts to form islands and Ir–Ta is observed at the sample surface. The silicon substrate did not react after 30 min annealing up to temperatures of 650 °C.

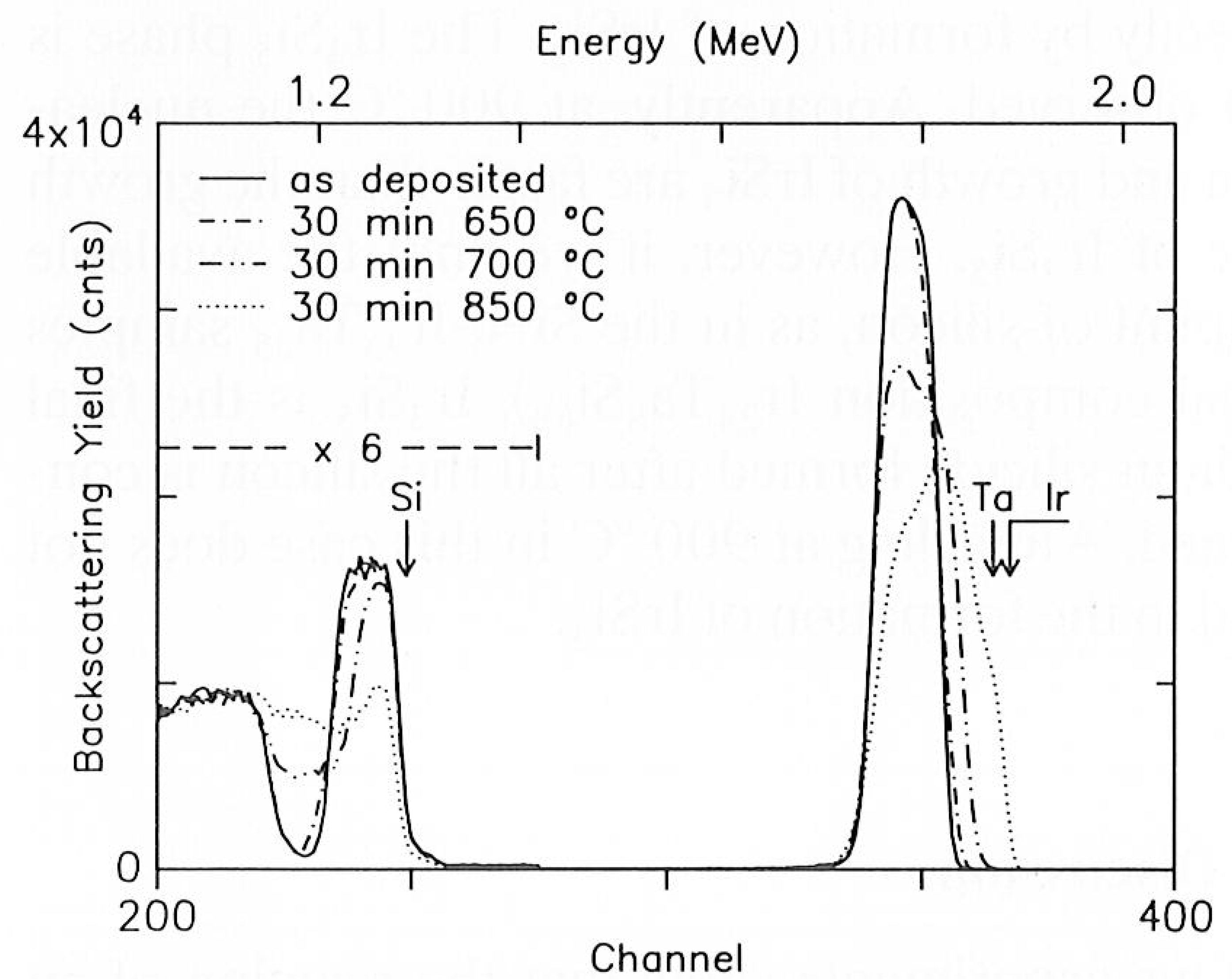

Fig. 5. RBS spectra of Si_3N_4–a-$Ir_{45}Ta_{55}$–Si samples. Sample tilt 0°, scattering angle 125°. Onset of reaction is observed at 650 °C. The first reaction step is at 700 °C. Full reaction occurs between 800 and 850 °C.

becomes significant at 700 °C. A 30 min anneal at 700 °C causes part of the silicon top layer and the underlying Ir–Ta to intermix: the width of the silicon surface peak decreases and a silicon signal between substrate and top layer appears. Also, the Ir–Ta signal broadens, decreases in yield and moves towards the surface peak position. After annealing at 850 °C, Ir–Ta appears at the sample surface and the silicon top layer has mixed almost homogeneously with the Ir–Ta.

Both XRD and TEM (not shown) on the Si_3N_4-c-$Ir_{75}Ta_{25}$–Si and c-$Ir_{75}Ta_{25}$–Si sample structures respectively reveal that an Ir(Ta) solid solution, some tantalum and amorphous silicon are present in the samples as deposited. Also,

after annealing the samples at the stated temperatures, both XRD and TEM yield the same results. Above 650 °C the amorphous silicon crystallizes and at 700 °C the reaction begins to form IrSi. After annealing for 30 min at 750 °C, $TaSi_2$ is observed. At 800 °C the silicon is further consumed and a second iridium silicide starts to form, Ir_3Si_5. At 850 °C (and 900 °C) the reaction quickly reaches completion and $TaSi_2$ and Ir_3Si_5 are the only phases observed.

The phase sequence in iridium silicide formation for thin film iridium on silicon substrates is as follows [20, 21]. At 400 °C IrSi forms, followed by Ir_3Si_5 at 500 °C, and both phases grow in a diffusion-limited process. At 1000 °C $IrSi_3$ nucleates. In comparison, our XRD observations and most clearly our TEM experiments on Si–a-$Ir_{45}Ta_{55}$ samples (see Fig. 2) show that upon reacting at 900 °C IrSi is formed first, followed directly by formation of $IrSi_3$. The Ir_3Si_5 phase is not observed. Apparently, at 900 °C the nucleation and growth of $IrSi_3$ are faster than the growth rate of Ir_3Si_5. However, if we limit the available amount of silicon, as in the Si–c-$Ir_{75}Ta_{25}$ samples (final composition $Ir_{24}Ta_8Si_{68}$), Ir_3Si_5 is the final iridium silicide formed after all the silicon is consumed. Annealing at 900 °C in this case does not lead to the formation of $IrSi_3$.

4. Discussion

Our experiments show that the reaction of an amorphous Ir–Ta diffusion barrier between silicon and aluminium occurs at a lower temperature for the aluminium interface than for the silicon interface. The reaction temperature of 550 °C at the aluminium interface is somewhat higher than the temperature at which a reaction between aluminium and tantalum occurs (values between 450 and 525 °C are reported [22, 23]). The reaction temperature between iridium and aluminium is not known, but it is expected to be lower than 500 °C following the trends in group VA and VIIIA metals [23]. Although formation of IrAl at lower temperatures would lower the energy of the system (see Table 1, reaction A), this reaction does not occur until 600 °C. These observations are consistent with the model that an amorphous alloy reacts with aluminium only at the temperature above which aluminium will react with both constituents (Table 1, reaction B). At this temperature aluminium penetrates the amorphous

TABLE 1 Several reactions mentioned in the text and their reaction enthalpy. To calculate ΔH_r the following heats of formation (in kJ (g atom)$^{-1}$) are used: a-$Ir_{45}Ta_{55}$ (−41), Ir(25% Ta) (−38) and Al_3Ta (−30) calculated using the Miedema model according to refs. 16, 24 and 25; IrSi (−38) and $TaSi_2$ (−38) after ref. 26; IrAl (−72) after ref. 27. As an example, the calculation of ΔH_r is elaborated in Appendix A for reaction D

A	a-$Ir_{45}Ta_{55}$ + Al → IrAl + Ta	$\Delta H_r = -17$
B	a-$Ir_{45}Ta_{55}$ + Al → IrAl + Al_3Ta	$\Delta H_r = -29$
C	a-$Ir_{45}Ta_{55}$ + Si → IrSi + Ta	$\Delta H_r = +7$
D	a-$Ir_{45}Ta_{55}$ + Si → IrSi + $TaSi_2$	$\Delta H_r = -18$
E	Ir(25% Ta) + Si → IrSi + Ta	$\Delta H_r = -7$
F	Ir(25% Ta) + Si → IrSi + $TaSi_2$	$\Delta H_r = -17$

alloy and reacts with the refractory metal and near-noble constituent simultaneously. This simultaneous formation reaction is in agreement with the observation that IrAl formation occurs only after the Al_3Ta begins to form. In comparison, the interface between the silicon and amorphous Ir–Ta is stable to at least 650 °C. This result suggests that amorphous $Ir_{45}Ta_{55}$ might be used as a sacrificial barrier layer up to temperatures of 650 °C for sufficiently thick layers to inhibit aluminium diffusion through the polycrystalline Al_3Ta–IrAl layer.

The high reaction temperature of 875 °C between (100) Si and a-$Ir_{45}Ta_{55}$ is remarkable. Although iridium reacts endothermically (Table 1, reaction C) with silicon between 400 and 500 °C to form IrSi [20], no reaction between silicon and amorphous Ir–Ta is observed at these temperatures. The iridium is kinetically restricted to the amorphous matrix, which has a more negative heat of formation than IrSi. Also, the reaction temperature to form tantalum silicides from tantalum and silicon is above 500 °C. However, at 650 °C, where tantalum silicides do form and silicon is thought to be mobile, the amorphous diffusion barrier is still stable. On the basis of thermodynamic calculations, either the formation of ternary compounds [8] or the highly exothermic reaction (Table 1, reaction D) to form tantalum and iridium silicides was expected to occur at 650 °C. Yet, neither of these processes is observed. Further, there is no evidence for crystallization of the a-$Ir_{45}Ta_{55}$ below 875 °C, at which temperature the reaction with silicon became significant. The amorphous and crystalline Ir–Ta alloys both have large negative heats of mixing and are therefore quite stable, and if the diffusion of silicon into and through the amorphous phase is very slow, then the reaction

becomes dominated by the slow kinetics of silicon diffusion. The a-$Ir_{45}Ta_{55}$ must decompose (at a temperature near the crystallization temperature) before silicon or iridium and tantalum are available for the reaction. This high decomposition temperature and slow silicon diffusion would agree with a high activation barrier to reaction and consequently a high reaction temperature.

The observations by Hörnström *et al.* [13] that only slight improvement is achieved when amorphous W–Re is applied as a diffusion barrier in Si–Al metallization schemes instead of its crystalline counterpart, and the results obtained by Hunt *et al.* [17] that the reaction temperature of the Si–$Ir_{55}Ta_{45}$ structure is much higher than the crystallization temperature of the amorphous alloy, suggest that amorphicity of buffer layers only plays a minor role in the stability of sandwich structures. Our results, however, show that amorphicity of the buffer layer does play a role. The $Ir_{45}Ta_{55}$ alloy remains amorphous when in contact with silicon and does not react until a temperature of 875 °C is reached. The crystalline $Ir_{75}Ta_{25}$ alloy, which consists mainly of an Ir(Ta) solid solution, reacts with silicon at around 700 °C. It is unlikely that the lowering of the reaction temperature is an effect of thermodynamics. Although the formation of IrSi by decomposing Ir–Ta in contact with silicon is an exothermic reaction (Table 1, reaction E), no reaction is observed at 400 °C, the temperature at which IrSi can form. At 700 °C, which is still higher than the reaction temperature between tantalum and silicon, both $TaSi_2$ and IrSi can form, as observed. This is an exothermic reaction (Table 1, reaction F) with almost the same heat of reaction as for the Si–a-$Ir_{45}Ta_{55}$ case (Table 1, reaction D). We believe that iridium is locked in the Ir(Ta) solid solution at low temperatures and therefore unable to react with silicon. At 700 °C silicon is highly mobile in the crystalline alloy and able to penetrate Ir–Ta via grain boundaries. This enables a reaction, although relatively slow in comparison with systems known from the literature, *e.g.* Pt–Ti [8]. At this temperature of 700 °C no interdiffusion takes place when amorphous $Ir_{45}Ta_{55}$ is in contact with silicon. We attribute this to the absence of grain boundaries and apparent lack of silicon diffusion. We did not study the Ir(Ta)–Al interface, but grain boundary diffusion of aluminium, which occurs at around 300 °C [4], is expected to lower the reaction temperature as observed for amorphous Ir–Ta and aluminium.

5. Conclusions

An extremely high reaction temperature between silicon and the amorphous metal alloy $Ir_{45}Ta_{55}$ of 875 °C has been found. The Ir–Ta alloy, which crystallizes at 900 °C, remains amorphous up to the reaction temperature. During the reaction, $TaSi_2$ and IrSi form. The IrSi transforms further into $IrSi_3$. The interface with the silicon substrate is smooth after annealing at 900 °C but rough at 1000 °C. An amorphous Ir–Ta alloy in contact with aluminium reacts at 550 °C, which is equal to the reaction temperature between tantalum and aluminium. At this temperature Al_3Ta and IrAl are formed. Although reaction between Ir–Ta and aluminium occurs at 550 °C, the silicon interface in Si–IrTa–Al sample structures remains unaffected up to temperatures of 650 °C. The reaction beween silicon and crystalline Ir–Ta starts at 700 °C, which is attributed to the influence of silicon diffusion via grain boundaries.

Acknowledgments

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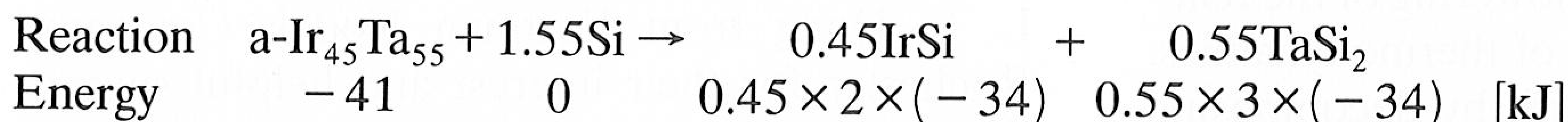
Appendix A

Reaction D from Table 1, the silicidation of a-$Ir_{45}Ta_{55}$, is elaborated as an example of how to calculate the heat of reaction. The reaction is balanced as follows:



Reaction	a-$Ir_{45}Ta_{55}$ + 1.55Si →	0.45IrSi	+ 0.55$TaSi_2$	
Energy	−41 0	$0.45\times2\times(-34)$	$0.55\times3\times(-34)$	[kJ]

The total heat release is $\Delta H_R=\{0.45\times2\times(-34)+0.55\times3\times(-34)\}-\{(-41)+0\}=-45.7$ kJ. To obtain the heat of reaction, ΔH_r, the total heat release, ΔH_R, has to be normalized to the total number of atoms involved, which is $0.45Ir+0.55Ta+1.55Si=2.55$ g atom. This yields $\Delta H_r=-45.7/2.55=-18$ kJ (g atom)$^{-1}$.