JOURNAL OF MATERIALS SCIENCE 28 (1993) 3155–3160

Behaviour of adsorbed oxygen during rapid electron-beam heating of Ta/Ti bilayers on single-crystal silicon

F. MAHMOOD, H. AHMED,
Microelectronics Research Centre, Cavendish Laboratory, Cambridge University, Madingley Road, Cambridge CB3 OHE, UK
M. SULEMAN
Centre for Solid State Physics, University of the Punjab, New Campus, Lahore 20, Pakistan

Silicidation of thin films of Ta/Ti bilayers on silicon substrates, in the temperature range 750–1000 °C, using rapid electron-beam heating is described. The redistribution of adsorbed oxygen in the metal films and its effect on the formation of the silicide is examined. It was found that the silicidation of the bimetallic films proceeded sequentially. First titanium and then tantalum layers were converted into their respective silicides. During the growth of titanium disilicide, adsorbed oxygen moved to the interface between the unreacted tantalum film and the grown titanium disilicide, where it formed a thin layer of silicon dioxide. The silicon dioxide barrier inhibited silicon diffusion and the tantalum layer only converted to silicide at temperatures higher than 750 °C which were maintained for a few seconds.

1. Introduction

There have been many investigations of new metallization schemes with low contact resistivity and high thermal stability on single-crystal silicon. The properties of multilayer structures consisting of refractory metals or their silicides, such as diffusion barriers, oxidation resistance, and electromigration resistance have been studied [1, 2]. It is well known that the silicidation of titanium by solid-phase reaction in a nitrogen ambient leads to a bilayer structure consisting of titanium nitride/titanium silicide [3]. The titanium nitride layer effectively acts as a diffusion barrier for silicon transport and, consequently, this technique is used to limit the lateral spread of titanium silicide in salicide technology [4]. It has also been reported that during the heating of an Si/Mo/Ti trilayer structure on a silicon substrate, where silicon and molybdenum are the sacrificial layers, the stability of titanium against oxidation improves [5].

Solid-phase reactions of thin films of refractory metal multilayers and alloys with silicon is also interesting from the metallurgical viewpoint. Such reactions are useful in understanding the transportation mechanism of material across different interfaces [6, 7]. In a study of the reaction of Pd–Ta alloy films on a silicon substrate, it has been shown that the reaction temperature depends on the composition of the alloy, being higher for a tantalum-rich alloy [8]. The Pd_2Si and $TaSi_2$ phases are separated after heating with the former phase, always making the inner silicide layer in contact with the silicon substrate. Owing to the out diffusion of palladium from the alloy, the film contained a high density of defects and the reaction temperature at which silicide was formed for pure tantalum was 400–500 °C. The reactions of Co–Ni alloy thin films [9] and Co/Ni bilayers (irrespective of the order) [10] with the silicon substrate are important illustrations of the nucleation process in the formation of disilicides. The pairs Co_2Si, Ni_2Si and $CoSi_2$, $NiSi_2$ are isomorphous and are totally miscible, whereas intermediate monosilicide phases CoSi and NiSi do not share the same structure and are immiscible [9, 10]. Therefore, phase separation occurs for monosilicides and the disilicide phase grows by nucleation as a solid solution $(Co–Ni)Si_2$ at the interface between the two immiscible monosilicides.

In this study, we report on the formation of multiple silicide thin films on a silicon substrate by the solid phase reaction in a Ta/Ti/Si system. Sheet resistances of the annealed layers were measured with a four-point probe. Auger electron spectroscopy was used for depth profiling. Scanning electron microscopy (SEM) and cross-section transmission electron microscopy (TEM) were carried out to study the effect of heating on the surface and at the interfaces between different films.

2. Experimental procedure

The substrates used were 7–20 Ω cm (111)-oriented p-type silicon wafers. All the substrates were degreased for a few minutes in boiling trichloroethylene, acetone and methanol consecutively. The wafers were then cleaned in a solution of sulphuric acid and

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hydrogen peroxide (3:1), and immersed in 10% buffered hydrofluoric acid. This was followed by a rinse in deionized water (1 MΩ) and the samples were blow-dried using a nitrogen gun. The samples were dipped in dilute hydrofluoric acid before insertion into the electron beam evaporator. Layers of titanium and tantalum each 55 ± 5 nm thick were deposited in sequence without breaking the vacuum. The deposition rate was kept at 10 nm min^{-1} with the base pressure maintained at 8×10^{-7} torr (1 torr = 133.322 Pa). The wafers were cut into 10 mm × 10 mm chips for heating and subsequent analysis.

The samples were placed in a chip carrier which holds them in thermal isolation, and then heated in a vacuum of 2×10^{-6} torr in an electron-beam annealing system. The system has been described in detail elsewhere [11]. Heating was carried out with a 20 keV electron beam incident on the back, unpolished side of the silicon substrate. The electron beam was incident over an area just larger than 1 cm^2 so that the samples were uniformly heated. For the silicidation process, heating was performed using an initial beam current density of 1.3 mA cm^{-2} (beam power 26 W cm^{-2}), giving ramp-up times of 2 and 4 s to reach temperatures of 750 and 1000 °C, respectively. The beam current drops in the transition from the ramp-up region of the thermal cycle to the steady state region where the input power balances the radiation loss. The temperature is kept at a constant value for a preset time. Typically, beam current densities necessary to keep the equilibrium temperature at 750 and 1000 °C are 0.25 and 0.75 mA cm^{-2}, respectively, which can be held for as long as the heating is maintained. To end the heating cycle, the beam is blanked automatically after the preset time and the sample cools by radiation. For short anneals, the total process time includes the ramp-up, dwell, and cooling times. For example, in the case where the peak temperature duration is 100 ms, the effective heating time for the reaction in the temperature range studied is estimated to be about 670 ms. Heating for times longer than 10 s can be considered to be effectively isothermal. In our experiments the total thermal budget was kept to a minimum and most of the reaction between the bilayers and the silicon substrate occurred while the temperature was near its maximum value. All the times quoted are the periods for which the peak temperatures were held constant. An optical two-colour pyrometer IRCON-R series was used to monitor the temperature, viewing the unpolished clear silicon rear-side of the specimen.

Auger depth profiles were obtained in a scanning Auger microprobe (Jeol-model JAMP-10S). A beam of 3 keV argon ions at a current of 10 μA was used to sputter the material by raster scanning the beam over an area 3 mm × 3 mm. A 10 keV electron beam at a current of 0.1 μA was used for Auger electron spectroscopy. The pressure during spectroscopic analysis was 7.5×10^{-10} torr. The proportions of tantalum, titanium, silicon, oxygen, carbon, and nitrogen were monitored. The surface topography of the samples before and after annealing was determined in a Hitachi S-800 scanning electron microscope. The interfacial study was carried out by transmission electron microscopy. Cross-sectional specimens were examined in a Jeol-2000 EX transmission electron microscope operating at 200 kV.

3. Results and discussions

The average sheet resistance of the as-deposited Ta/Ti bilayers on the silicon substrate was 15.5 Ω/□. Fig. 1 shows the dependence of the sheet resistance on annealing temperatures and times. After heating at 750 °C for a dwell time of 1 s, the sheet resistance dropped to a value of about 3.5 Ω/□ and then remained at this value for longer heating times. The stable values are consistent with an essentially unreacted tantalum layer in contact with a fully formed titanium silicide film. After heating at 800 °C for dwell times between 1 and 30 s, the sheet resistance remained constant at the same values as were obtained at 750 °C, but the values decreased to about 1.4 Ω/□ for times between 30 and 90 s. This is in accord with the involvement of the tantalum film in the reaction as was determined by the AES depth profiling. Heating the bilayers at 900 °C for dwell times > 1 s converted the metal films into both $TaSi_2$ and $TiSi_2$ and the sheet resistance decreased to a minimum value of 1.4 Ω/□.

Scanning electron microscopy was used to investigate the surface conditions of the bilayers after annealing at different temperatures. Fig. 2 shows a planar scanning electron micrograph and a dark-field cross-sectional transmission electron micrograph of the as-deposited films and planar scanning electron micrographs of the layers annealed at 800 °C for dwell times of 10 and 90 s. The surface texture of the layers annealed for 10 s shows granular features (Fig. 2c) similar to those seen in the micrograph (Fig. 2a) of the unreacted sample. This implies that the upper film consisted of unreacted tantalum and the lowering of the sheet resistance is due mainly to the conversion of titanium layers into silicide. After heating for 90 s (Fig. 2d), the layers displayed a surface roughness characteristic of grain growth in the silicide. The

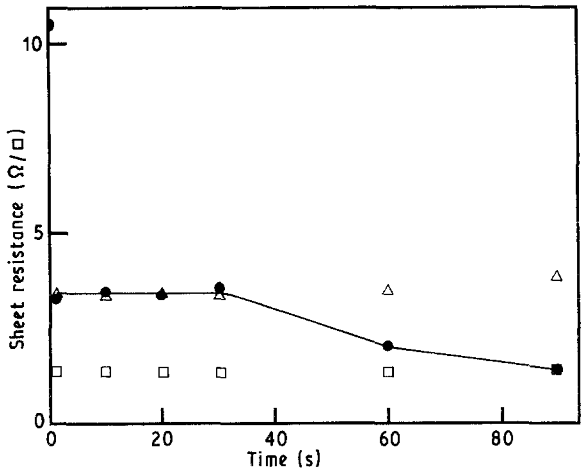

Figure 1 The variation of the sheet resistance of a Ta/Ti bilayer on a silicon substrate as a function of temperature and dwell time. (△) 750 °C, (●) 800 °C, (□) 900 °C.

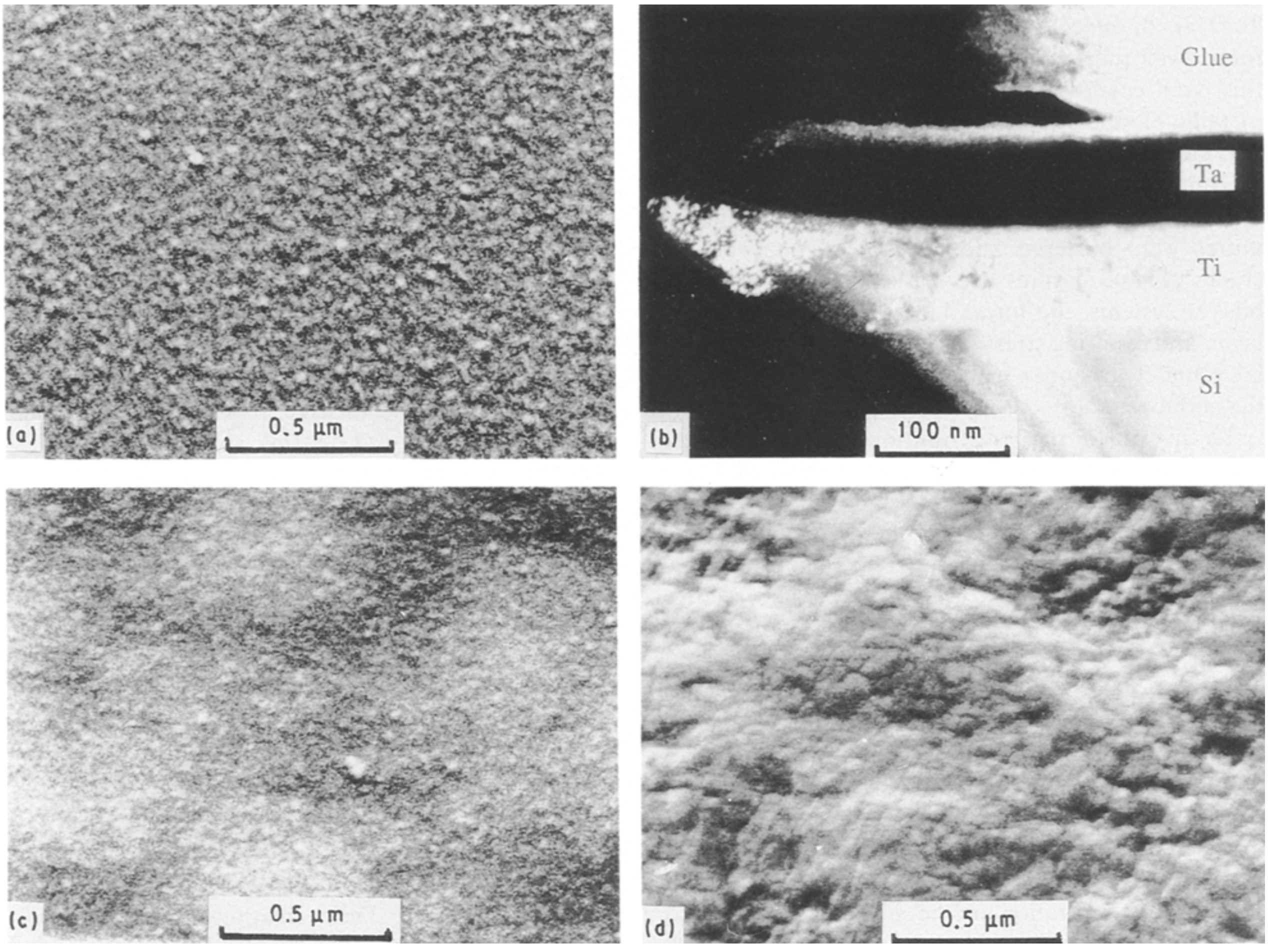

Figure 2 (a, b) Scanning electron and dark-field transmission electron micrographs showing planar and cross-sectional views of the as-deposited Ta/Ti bilayer on the silicon substrate. (c, d) Scanning electron micrographs showing the surface topography of the bilayer after heating at 800 °C for dwell times of 10 and 90s.

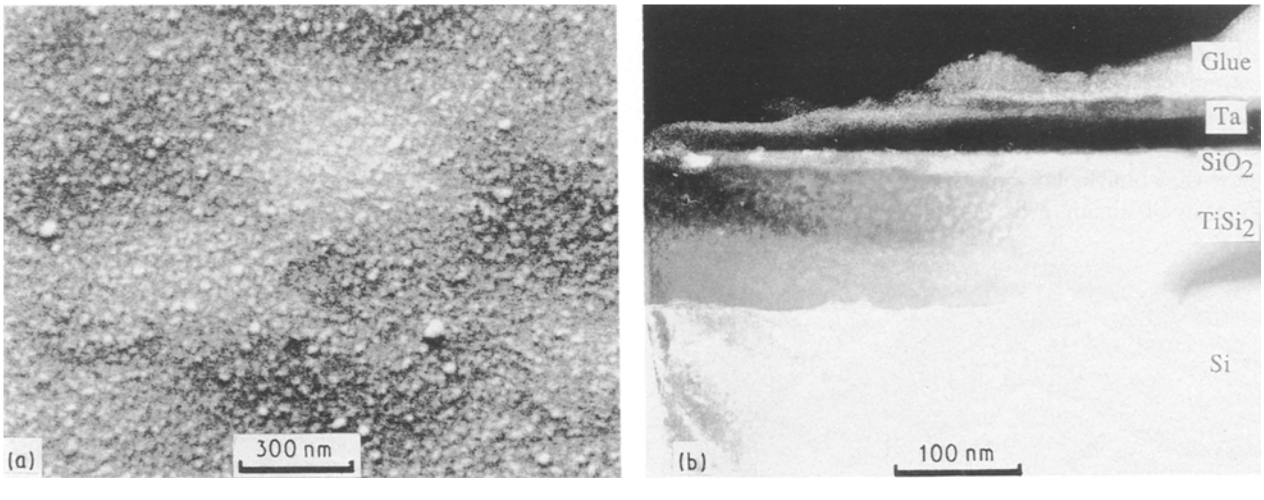

Figure 3 Scanning electron and dark-field transmission electron micrographs showing the planar and cross-sectional views of the Ta/Ti bilayer on silicon after heating at 900 °C for a dwell time of 100 ms.

samples heated at 900 °C for a dwell time of 100 ms were examined by SEM and cross-sectional TEM as shown in Fig. 3. The scanning electron micrograph showed the surface to be as for the unreacted tantalum film. The dark-field cross-sectional transmission electron micrograph (Fig. 3b), however, revealed the interfaces in detail. The fully grown titanium disilicide has a sharp interface with the silicon substrate, whereas a band appeared between the unreacted tantalum film and the grown titanium disilicide. It can be seen that this band has a relatively wavy interface with the titanium silicide. The AES depth profiling indicated that about 20%–24% oxygen accumulated at the Ta/$TiSi_x$ interface after heating the bilayer at 900 °C for a dwell time of 100 ms. Therefore, it is likely that this band consists of a complex compound of either metallic or silicon oxides.

Dramatic changes in the surface texture of the bilayers were observed after heating at 1000 or 1100 °C. Most of the layers heated at these temperatures were blistered and developed a network of cracks. These features are shown in Fig. 4. In the bilayer systems, the formation of silicide in the first layer, and resulting stress in that layer, puts the second layer under tension, which upon relaxation, damages the surface.

To investigate the redistribution of oxygen, Auger depth profiles of selected samples were obtained. Fig. 5 shows the Auger depth profiles of unreacted and reacted samples. An estimation of the concentration of oxygen in the bimetallic layers on the silicon substrate is made using the peak to peak heights and relative sensitivity factors of elements detected in the Auger profiles [12]. The average relative concentration of oxygen in the unreacted titanium layer is $\sim 5\%$ increasing to $\sim 24\%$ at the interface and then decreasing to $\sim 3\%$ in the outer tantalum layer (Fig. 5a). After heating at 750 °C for a dwell time of 100 ms (Fig. 5b), the titanium layer is partly converted to silicide of uniform composition. From the Auger depth profile it is seen that oxygen is redistributed with a $< 5\%$ concentration in the silicide, increasing to $\sim 21\%$ at the Ta/Ti interface. After annealing at 800 and 900 °C for a dwell time of 100 ms, the titanium layers are fully reacted and the tantalum films remain unreacted. Oxygen is seen to be accumulated at the Ta/$TiSi_2$ interface (Fig. 5c, d). Fig. 5e shows an AES depth profile of a sample annealed at 1000 °C for a dwell time of 90 s. Both the titanium and tantalum layers are completely converted into their respective silicides, with the $TiSi_2$ as the inner layer. Interestingly, oxygen still remains at the interface between the two silicides, although, its content has been decreased to about 5%. These observations support the view that interfacial oxygen has drastic effects on the kinetics of silicide growth [6].

These results have demonstrated that titanium and tantalum layers reacted independently with silicon to form silicides and that silicon is the major diffusing species in the reaction. However, the diffusion of silicon into the tantalum film is inhibited by interfacial oxygen. We have considered the nature of the barrier formed at the interface between the tantalum film and the grown $TiSi_2$. It has been shown in the ternary phase diagrams of the Ti–Si–O and Ta–Si–O systems that $TiSi_2$ and $TaSi_2$ are stable in contact with SiO_2 [13]. During the oxidation of $TiSi_2$ on a silicon substrate, if silicon diffuses rapidly through the silicide to the oxidizing interface, then SiO_2 rather than TiO_x is formed. Under rapid thermal annealing at high temperatures, as involved in this study, simultaneous redistribution of oxygen adsorbed in the titanium films and fast diffusion of silicon through the first silicide layer to the Ta/Ti interface favours the formation of an interfacial silicon dioxide barrier layer rather than TaO_x or TiO_x. Beyers [13] confirms that no stable TaO_x or TiO_x phases exist in the Ti–Si–O and Ta–Si–O systems, and in our results in Fig. 3b, the SiO_2 barrier is clearly shown to be formed at the Ta/$TiSi_2$ interface. For the subsequent silicidation of the tantalum overlayer, the SiO_2 barrier has to be reduced. However, in a recent paper [14] on the reactions of bilayers of refractory films with the SiO_2 substrate, it was reported that the tantalum films did not react with an SiO_2 substrate even for an anneal at 1000 °C for 30 min. The formation of $TaSi_2$, in our study, at temperatures > 750 °C for dwell times of a few seconds is surprising. We believe that the thinness and non-homogeneity of the SiO_2 interfacial barrier allowed the transport of silicon thus allowing tantalum silicide to be formed.

4. Conclusions

It has been shown that low-resistivity bilayers of $TaSi_2$/$TiSi_2$ on silicon can be formed by the solid-phase reactions during a rapid thermal annealing

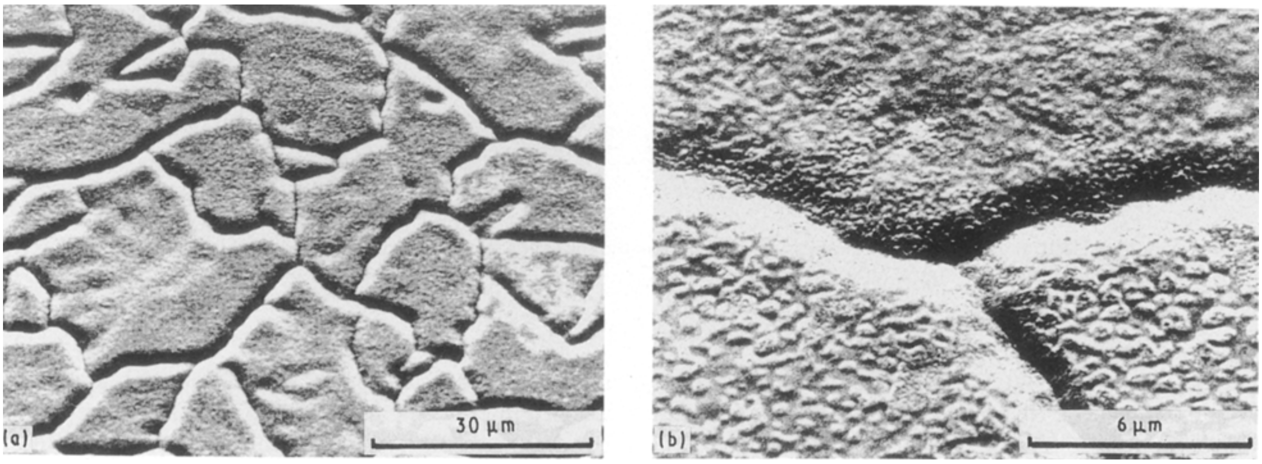

Figure 4 Scanning electron micrographs showing blistering of the silicides formed after heating the Ta/Ti bilayer on silicon at 1000 °C for a dwell time of 100 ms.

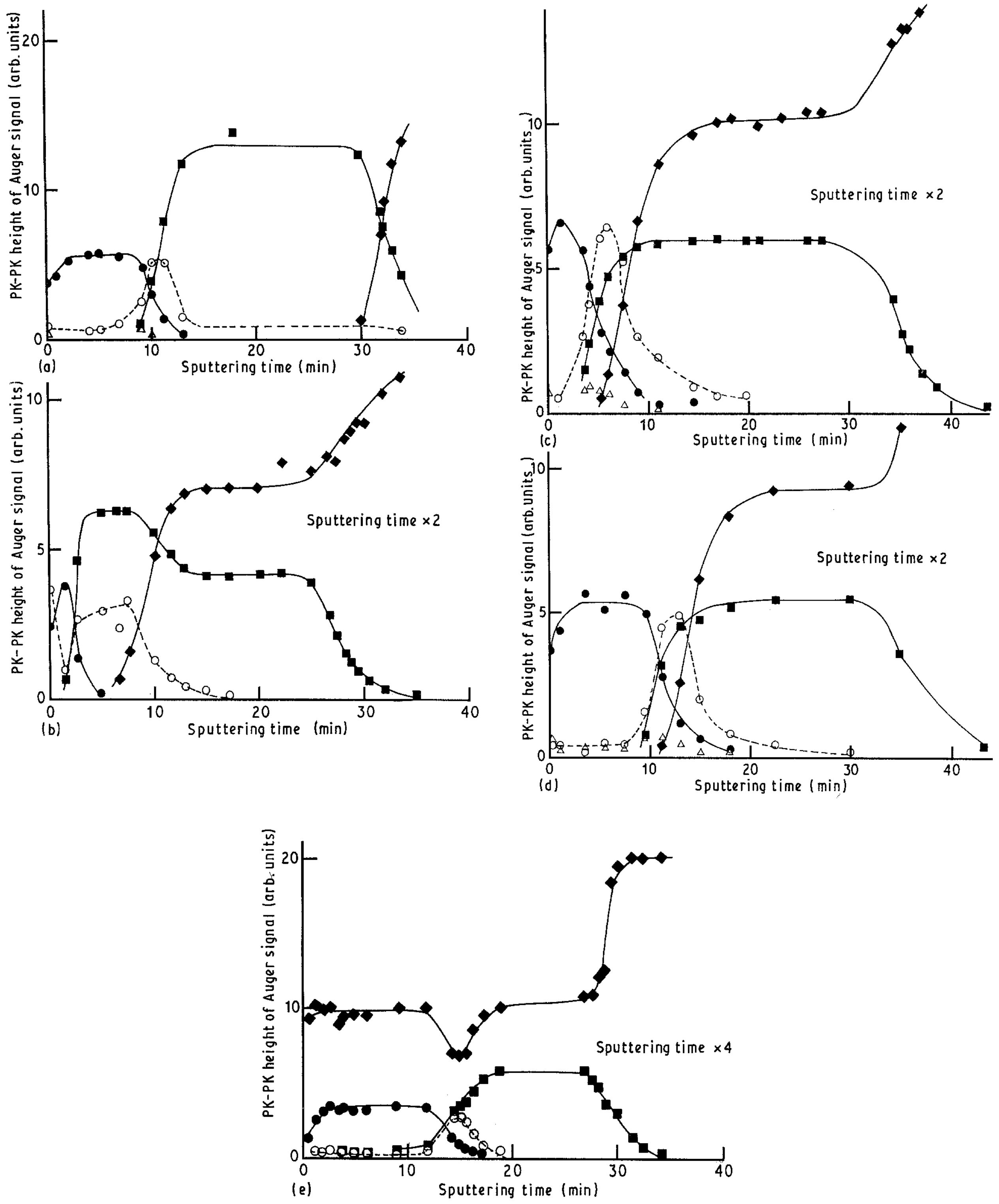

Figure 5 The AES depth profiles of the Ta/Ti bilayer on the silicon substrate: (a) As-deposited, and after heating at (b) 750 °C, (c) 800 °C, (d) 900 °C for a dwell time of 100 ms. The profile (e) shows the transformation of both the metal layers into their respective silicides after heating at 1000 °C for a dwell time of 90s. (◆) Si (*L V V*) 92 eV, (■) Ti (*L M M*) 418 eV, (●) Ta (*N V V*) 179 eV, (△) C (*k L L*) 272 eV, (○) O (*K L L*) 510 eV.

process. However, the growth of these refractory metal silicides in stacks on the silicon substrate follows a complex path. The differing thermal properties of the silicide layers, large volume changes due to silicide growth, and the development of strain make the kinetics of the reaction unpredictable. It was shown that the presence of oxygen in the as-deposited Ta/Ti bilayer retarded the growth of tantalum silicide by forming a silicon dioxide barrier at the Ta/Ti interface. Silicon was found to be the main diffusing species in the reaction while tantalum or titanium atoms remained stationary. Annealing the layers at 750, 800 and 900 °C for a dwell time of 100 ms resulted in the formation of only titanium silicide with the tantalum layers unreacted. Increasing the temperatures to 1000 °C, which was maintained for 90 s, transformed the Ta/Ti/Si system into the $TaSi_2/TiSi_2/Si$ structure, with a relatively low concentration of oxygen, i.e. 5%, retained at the interface between the two silicides. The metallurgical failure of the silicide layers, obtained at

1000 or 1100 °C, is attributed to stress relaxation in the layers.

Acknowledgements

We thank D. Sarkar for depositing the metal films used in this study. F. Mahmood acknowledges a Central Overseas Training Scholarship from the Government of Pakistan.

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Received 8 October 1991
and accepted 25 June 1992