JOURNAL OF MATERIALS SCIENCE 20 (1985) 341–345

The solution growth of silicide layers on molybdenum substrates

R. YAZDANI-RAD, C. A. HOGARTH
Department of Physics, Brunel University, Uxbridge, Middlesex, UK

A saturated solution of silicon in molten tin is employed to grow a silicide layer on molybdenum substrates. The growth is carried out in a chamber analogous to a vertical liquid-phase epitaxy system by dipping the rotating substrate into the melt at temperatures in the range 900 to 1000° C, and using different dipping times of up to 60 min. By X-ray diffraction analysis, the deposits appear to contain only molybdenum disilicide ($MoSi_2$). Examination by other characterization techniques such as optical microscopy, scanning electron microscopy and electron probe microanalysis give the layer thickness in the range 3 to 20 μm, and the silicide grain size of the order of 0.1 μm. Deposited layers appear as a rough-surfaced agglomeration of silicide grains with occasional cracks probably formed on cooling. The grains are generally equi-axed and efficiently packed into a film of fairly low porosity, there seems to be a linear correlation between layer thickness and deposition time. This suggests that the kinetics of $MoSi_2$ formation by this technique may be controlled by the rate of the interface reaction at the metal–silicide interface.

1. Introduction

For many years there has been a growing interest in the deposition of polycrystalline silicon (poly-Si) on various substrates. The direct deposition of silicon in thin layer form was initially proposed for use in solar cells [1–4], though in recent years a number of other semiconductor devices have shown new applications of such layers [5, 6].

An important factor in all these applications is the nature of the interface layer formed during the deposition process. For example, experiments using carbon substrates suffered from insulating SiC formed at the interface, and this made the deposit unsuitable for solar cell applications. On the other hand it is anticipated that the use of a transition metal instead of carbon, could result in a conducting interface since most transition metal silicides are metallic conductors [7].

Silicides have been widely investigated because of their use in the electronics industry as ohmic contacts and as Schottky barriers [7, 8], as well as their various other applications, e.g. anti-oxidation coatings [9]. Nevertheless, there is little in the published literature concerning silicide formation during the deposition of silicon on metal substrates.

In this work, a molten-metal solution growth technique (dip-deposition) has been used to grow silicide layers on molybdenum substrates. The layers were then characterized using X-ray diffraction, optical microscopy, scanning electron microscopy (SEM), and electron probe micro-analysis (EPMA).

2. Experimental procedures

Dip-deposition may be considered as a modification of the well-known liquid-phase epitaxy (LEP) [10]. The apparatus employed in the present study was analogous to vertical LPE systems. However, in this case the substrate plane was parallel to the vertical rotation axis rather than being perpendicular to it as in the case of conventional LPE systems. The main part of the apparatus which is shown schematically in Fig. 1, consisted of a resistance-heating furnace capable of being operated at temperatures up to 1400° C. The temperature was maintained at ± 1° C using a Pt/Pt–13% Rh thermocouple and a controller to

0022–2461/85 $03.00 + .12 © *1985 Chapman and Hall Ltd.*

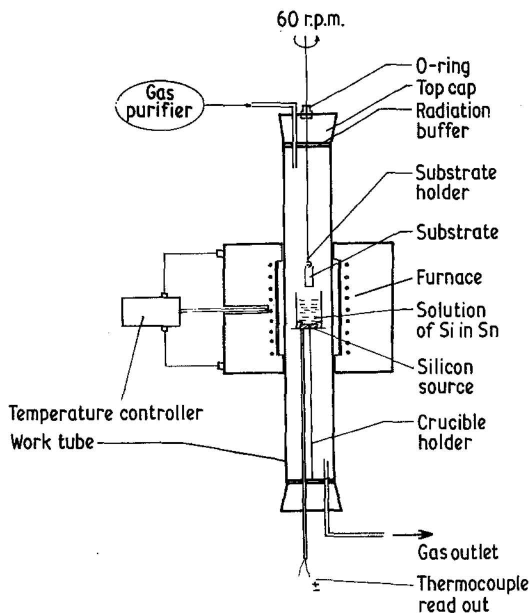

Figure 1 Schematic diagram of the dip-deposition apparatus.

control the power feed to the furnace winding. The melt temperature was monitored during the deposition using another thermocouple attached to the bottom of the crucible. The work tube, crucible, crucible holder and the substrate holder were all made of fused silica. The deposition chamber was continuously flushed with high purity (99.996%) argon, which was made to flow from top to bottom through the system.

Tin was used as the solvent for silicon because of its availability, low melting point, low vapour pressure, and relative ease of separation from the deposition products. The binary phase diagram of Sn–Si [11] shows a slight solubility at low temperatures around the melting point of Sn. However, the solubility increases exponentially as the temperature is raised; at 1000° C about 3% Si can be dissolved in tin. Saturation was attained by leaving the melt in contact with a piece of semiconductor-grade silicon at the desired temperature for about 4 h prior to dipping. The silicon was maintained in the lower part of the crucible as a source of solute atoms for the entire deposition period.

Substrates were 4 cm x 1 cm in size, cut from a 1.15 mm thick, 99.98% pure molybdenum sheet. The impurities expressed in at% were 0.009 W, 0.007 Fe, 0.002 N, with other elements 0.002.

Deposition was carried out in the chamber mentioned earlier. The substrate was kept just above the melt for a few minutes to ensure thermal equilibrium, then it was dipped and rotated at a rate of 60 rpm about the vertical axis. At the end of the run, the deposition was terminated by withdrawing the substrate, after which the entire chamber was slowly cooled to room temperature. To obtain the optimum deposition conditions, a number of preliminary experiments were carried out at various melt temperatures in the range 800 to 1050° C. Temperatures in the range 900 to 1000° C were found to yield more reproducible results, so the main experiments were accomplished at this temperature range.

Nickel-filtered Cu$K\alpha$ radiation ($\lambda = 0.1541$ nm) from a Philips PW 1410 X-ray unit was employed to obtain information on the chemical composition of the deposits. Diffractometer scans at 2θ values of 20° to 70° were performed; all patterns were obtained under identical conditions regarding the accelerating votage, tube current and slit size. An attempt was also made to assess semiquantitatively the extent of silicide formation by referring all peak heights in the X-ray spectra to (1 1 3) reflections from a small, thin piece of pressed α-Al_2O_3 powder (as an internal standard) placed on the specimen surface in the centre of the X-ray beam.

The X-ray results were supplemented by SEM and EPMA employing Cambridge, Stereoscan S_4 equipment and using accelerating voltages up to 20 kV.

3. Results and discussion

3.1. Composition

For all samples prepared in the temperature range of interest, the results of EPMA indicated the formation of a fairly uniform layer of a silicon compound as shown in Figs. 2a and b. These results were confirmed by X-ray diffraction analysis. A typical X-ray pattern of the deposit is shown in Fig. 3.

Although according to reference data on the Mo–Si binary system, molybdenum forms three binary compounds Mo_3Si, Mo_5Si_3 and $MoSi_2$ with silicon, molybdenum disilicide was the only phase detected in our experiments by the X-ray diffraction technique. This was the case for all samples prepared at 900, 950 and 1000° C, with various dipping times up to 60 min, the only change being the amount of silicide formed during the dipping.

Mechanisms involved in the formation of silicide layers by other processes, e.g. chemical

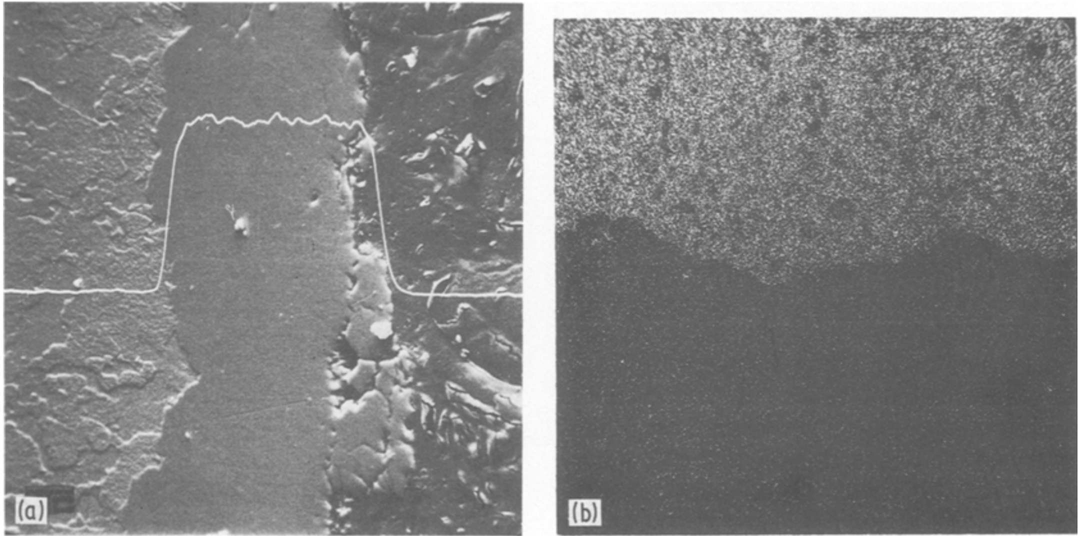

Figure 2 (a) Si$K\alpha$ X-ray line probing the Mo–$MiSi_2$ interface (polished specimen × 1000). (b) X-ray image of the same area of silicon as in (a).

vapour deposition (CVD) and sputtering, have previously been discussed by various authors [7, 8, 12]. Metal–silicon binary compounds can form by solid-state metallurgical reactions at temperatures far below their eutectic temperatures and silicon is usually the predominant diffusing species. At lower temperatures silicide formation first proceeds by diffusion of silicon into the metal; this leads to the formation of the most metal-rich silicide. As the temperature is increased transformation into more silicon-rich phases occurs.

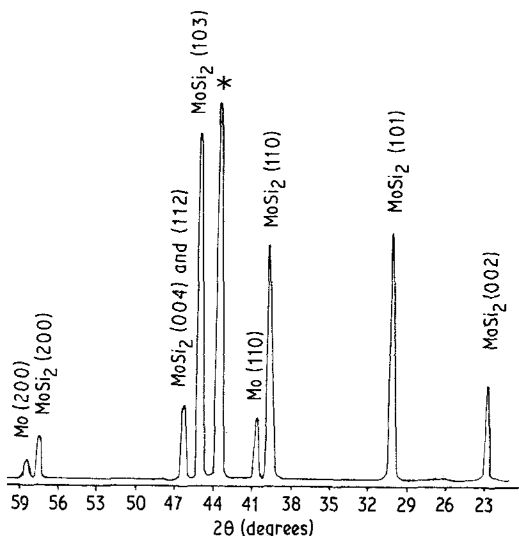

Figure 3 Typical X-ray diffraction pattern of the dip-deposited layers. Peak indicated * is the internal standard.

For sufficiently high temperatures, as employed in the present work, diffusion is so facilitated, that the reaction leading to the formation of the most silicon-rich compound occurs immediately, giving rise to the appearance of $MoSi_2$ alone as the end product.

3.2. Morphology and layer thickness

The layers had the appearance of the example shown in Fig. 4a. The SEM micrograph illustrates the film as a rough-structured agglomeration of silicide grains with occasional cracks probably formed on cooling. A higher magnification shown in Fig. 4b reveals a basic crystallite size of the order of 0.1 μm. The crystallites are generally equi-axed and efficiently packed into a film of rather low porosity. Their surface appearance is analogous to that of films obtained by Motojima *et al.* [9] by chemical vapour deposition. The cracks, however, seem to be shallower and there are far fewer of them in a unit area of the film.

An estimate of layer thickness for all specimens was obtained using the X-ray penetration depth and the following equation whose derivation can be found in various text books.

$$I = I_0 \exp\left(\frac{-2\mu x}{\sin\theta}\right) \tag{1}$$

I is the observed diffracted intensity from a coated substrate corresponding to a Bragg angle 2θ. I_0 is the intensity of the same diffraction line from an

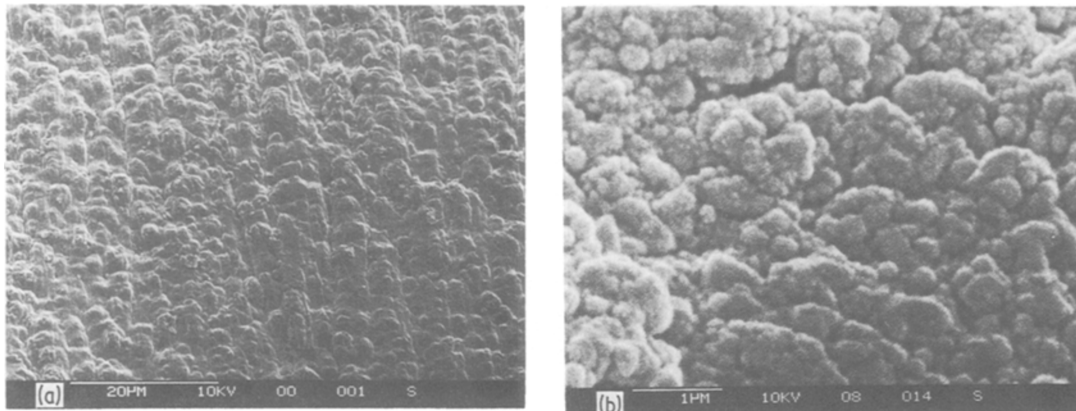

Figure 4 (a) Surface appearance of the deposits showing rough-surfaced agglomeration of $MoSi_2$ grains. (b) The same granular specimen of $MoSi_2$ at higher magnification.

uncoated substrate, and μ and x are the linear absorption coefficient and thickness of the deposit respectively. Using the above equation, values of the range 3 to 20 μm were obtained for the thickness of layers formed under various deposition conditions. The results are illustrated in Fig. 5 as plots of thickness versus dipping time at the three melt temperatures employed. They show a more or less linear dependence between film thickness and growth time. This behaviour, which is a characteristic of reaction–rate-limited growth [8, 12], suggests that the overall rate of $MoSi_2$ deposition by the present technique is governed by the rate of interface reaction leading to the formation of the silicide compound. Generally speaking, it is believed that solution growth of silicides by the present process proceeds with the following mechanism:

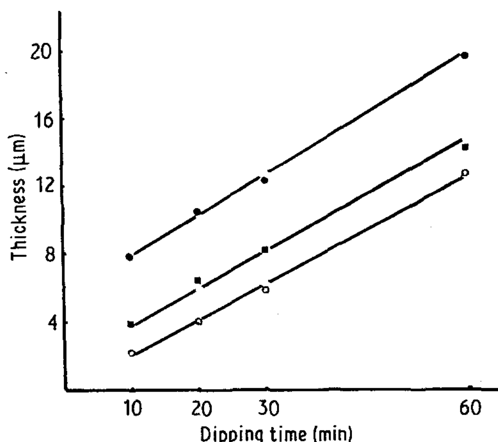

Figure 5 Variation of layer thickness with melt temperature and dipping time. • 1000° C; ▪ 950° C; ○ 900° C.

1. During the growth, the solution is always saturated, i.e. the concentration of silicon in the melt at any moment during the growth is that of the liquidus line in the Sn–Si system. This is a reasonable assumption since the presence of a solid silicon source in the bottom of the melt, and the fact that the melt is stirred during the deposition run, prevents it from being undersaturated or oversaturated.

2. The entire growth process occurs in four stages.

(a) Mass transfer of solute (silicon atoms) to the edge of a thin boundary layer in the melt ahead of the solid–liquid interface. The width of this boundary layer (sometimes called "the unstirred layer") depends on the kinematic viscosity of the melt, the angular rotation speed of the substrate and the diffusion coefficient of solute in the melt [13].

(b) Diffusion of solute atoms through the boundary layer.

(c) Diffusion of solute atoms through the already formed silicide layer.

(d) Solid-state reaction at the substrate–silicide interface leading to silicide formation.

Considering the linear dependence of layer thickness on the deposition time, the final stage (d) seems to control the rate of the silicide growth in our experiments.

Acknowledgements

The work includes some results obtained by the authors in the Materials and Energy Research Centre, Vanak, Tehran, and we acknowledge with

thanks the facilities made available to us there. For recent technical assistance we acknowledge the help of Mr P. Branscombe (Materials Technology Department) and Mr R. Bulpett (Experimental Techniques Centre) of Brunel University.

References

1. C. W. MUELLER and P. H. ROBINSON, *Proc. IEEE* **52** (1964) 1487.
2. H. SCHLÖTTERER and Ch. ZAMINER, *Phys. Status Solidi* **15** (1966) 399.
3. T. L. CHU, *J. Vac. Sci. Technol.* **12** (1975) 912.
4. C. FELDMAN, F. G. STAKIEWICZ and N. A. BLUM, *Thin Solid Films* **90** (1982) 461.
5. P. RAI-CHOUDHURY and P. L. HOWER, *J. Electrochem. Soc.* **120** (1973) 1761.
6. G. J. CAMPASI, A. J. BEVOLO, H. R. SHANKS and F. A. SCHMIDT, *J. Appl. Phys.* **52** (1981) 5043.
7. S. P. MURARKA, *J. Vac. Sci. Technol.,* 17 (1980) 775.
8. G. OTTAVIANI, *ibid.* **16** (1979) 1112.
9. S. MOTOJIMA, H. YOSHIDA and K. SUGIYAMA, *J. Mater. Sci. Lett.* **1** (1982) 23.
10. "Crystal Growth", edited by B. R. Pamplin (Pergamon Press, Oxford and New York 1975) p. 453.
11. M. HANSEN, "Constitution of Binary Alloys" (McGraw-Hill, Basingstoke and New York, 1958).
12. K. E. SUNDERSTRÖM, S. PETERSSON and P. A. TOVE, *Phys. Status Solidi (a)* **20** (1973) 653.
13. J. A. BURTON, R. C. PRIM and W. P. SLICHTER, *J. Chem. Phys.* **21** (1953) 1987.

Received 12 March
and accepted 27 March 1984