

Chemical vapour deposition of tantalum silicide thin films from difluorosilylene and tantalum halides

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Thin films of TaSi_x have been grown on Si(111), SiO₂ and graphite by LPCVD using SiF₂ and TaX₅ (X=F, Cl) as the precursors. Thin films prepared at 190–300 °C contained polycrystalline TaSi₂; 190 °C is the lowest temperature reported for the CVD preparation of TaSi₂. The compositions of the thin films were found to be 50% TaSi₂ and 50% amorphous silicon (a-Si).

Group IV, V and VI transition metals form a variety of compounds with silicon.¹ These silicides have many interesting properties, such as low resistance, high-temperature stability, high melting point, low density and good resistance to oxidation.²

In recent years, there have been a number of papers dealing with the synthesis of the metal silicides. It was reported³ that CoSi, β-FeSi₂ and MnSi–Mn₅Si₃ thin films are deposited by metal–organic chemical vapour deposition (MOCVD) using the precursors [Co(CO)₄(SiH₃)₂], [Fe(CO)₄(SiH₃)₂] and [Mn(CO)₅(SiH₃)], respectively. At the same time Kehr⁴ reported that Ta₅Si₃ thin films can be deposited by atmospheric pressure chemical vapour deposition (APCVD) at 1373 K using SiCl₄ and TaCl₅ as the precursors. It was later reported⁵ that TaSi₂ thin films were formed by low pressure chemical vapour deposition (LPCVD) using TaCl₅ and SiH₄ as the precursors.

Difluorosilylene, SiF₂, is known to grow amorphous silicon (a-Si) thin films at 400 °C. We have reported that thin films of TiSi₂ can be made by the reaction of SiF₂ and TiCl₄ at 500 °C,⁶ which is the lowest temperature at which titanium silicide thin films can be synthesized, indicating that silylene is a good choice for making silicon-containing thin films. We are currently exploring the scope of this method. In this paper we report the reaction between difluorosilylene and tantalum halides.

Experimental

The TaSi_x thin films were grown in a hot-wall LPCVD reactor. The experimental setup is shown in Fig. 1. The reactor consisted of a 30 mm diameter removable quartz tube connected

to an SiF₂ generation chamber. The SiF₂ was generated by the reaction of SiF₄ and Si at 1150 °C. TaF₅ and TaCl₅ (Strem, Newbury Port, MA) were used as received. The substrates used were Si(111), graphite and SiO₂. Thin films grown on graphite substrates were used for composition measurements while those grown on SiO₂ substrates were used for resistance measurements. The substrates were cleaned using standard procedures to remove grease and the oxide was etched off just before loading. The substrate temperature was measured with a K-type TC gauge.

The general procedure for a deposition run was as follows. First, the system was evacuated to 10⁻² Pa. Then the reactor and the SiF₂ generation chamber were heated to the desired temperatures. The system was then evacuated to 10⁻³ Pa, the SiF₄ gas was introduced into the SiF₂ generation chamber at room temperature and the metal source was vaporized into the reactor at 150 °C for TaF₅ and at 250 °C for TaCl₅. The deposition temperatures were controlled at 150–300 °C, and the deposition period was 2 h. Some thin films were annealed at 800 °C under an Ar atmosphere. IR experiments were carried out using an *in situ* IR instrument that consisted of an IR absorption cell and an SiF₂ generation chamber with a metal halide inlet (Fig. 2). The IR spectra were measured immediately after mixing.

Scanning electron microscopy (SEM) was performed in a JOEL 840A microscope, with energy dispersion X-ray analytical (EDXA) capability. X-Ray diffraction (XRD) patterns of the thin films were taken with Cu-Kα radiation using a Siemens D5000 diffractometer. The compositions of the samples were analysed by energy dispersive spectroscopy (EDS) both as-

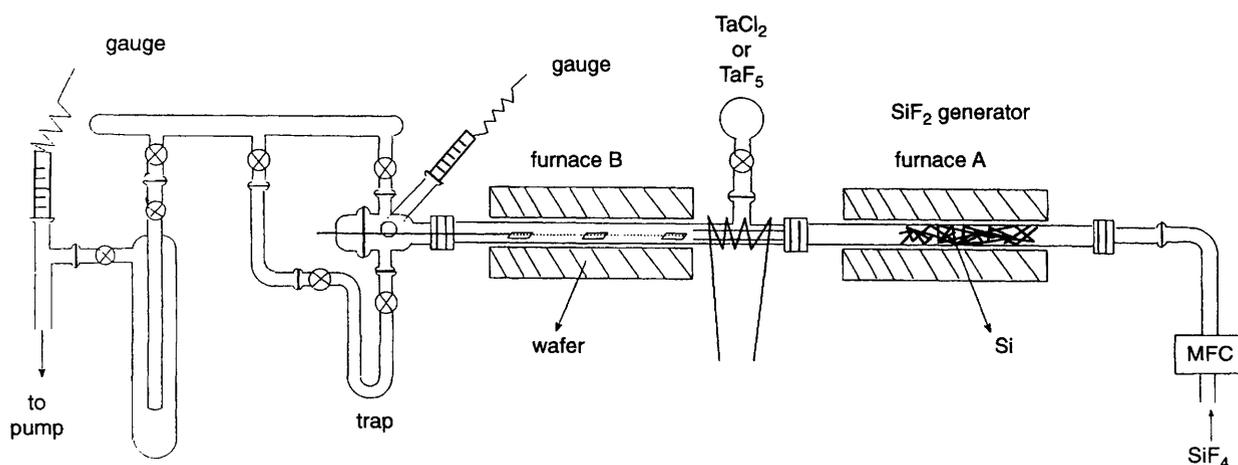


Fig. 1 Schematic diagram of the LPCVD hot-wall reactor

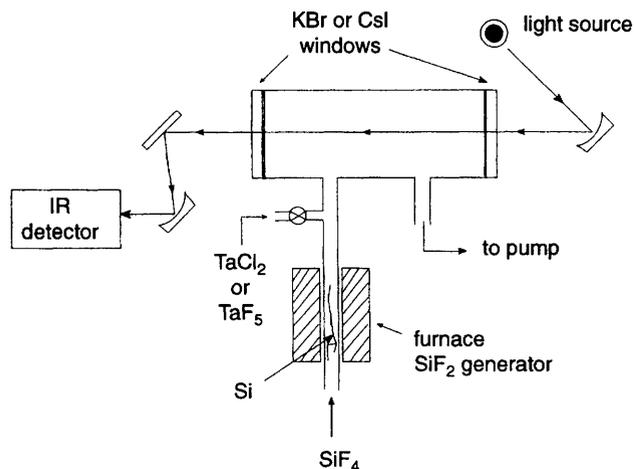


Fig. 2 Schematic diagram of the *in situ* IR system

deposited and after annealing, and several samples were also analysed by Auger electron spectroscopy (AES). IR spectra were obtained on a Perkin-Elmer PC2000 IR spectrometer. The resistance was measured by using an ac four-point probe.

Results and Discussion

Thin films grown on Si(111), SiO₂ and graphite from different metal sources and SiF₂ were characterized by SEM to determine the morphology and by EDS to determine the compositions. No significant differences were found between the thin films prepared from different metal halides. Fig. 3 shows the SEM images of the surfaces formed under different reaction conditions. In the films deposited at 190 °C, the particles are spherical with sizes ranging from 1 to 5 μm. The particles of the thin films synthesized at 300 °C have sizes in the range 1–2 μm [Fig. 3(a) and (b)]. The particle sizes decreased as the

deposition temperature was increased. Micrographs of thin films after annealing at 800 °C are shown in Fig. 3(c) and (d). Clearly, the particle sizes became smaller after the thin films were annealed. The EDS peaks revealed that the concentrations of Si and Ta in the thin films were 75% and 25%, respectively. According to the AES depth profile, the oxygen content dropped below 1 atom% after 10 min of sputtering. The fluorine content was negligible throughout the profile.

Fig. 4 shows the XRD patterns of thin films both as-deposited and after annealing. The broad XRD peaks at $2\theta = 25.4$ and 40.1° , which were assigned to TaSi₂(101) and (111) planes, were observed for the as-deposited thin film on the Si(111) substrate at 190 °C. This observation indicates that a polycrystalline TaSi₂ film started to form at 190 °C, the lowest temperature at which a TaSi₂ thin film has been reported to form. After annealing at 800 °C, thin films on Si(111) showed sharper peaks that are typical of TaSi₂ XRD patterns; all these peaks could be indexed to the hexagonal TaSi₂ C40 structure in the JCPDS file.⁷ The peaks at $2\theta = 21.25, 25.40, 34.82, 37.62, 40.13, 43.68, 46.97, 60.73, 66.10, 69.47$ and 74.49° belong to the (100), (101), (102), (110), (200), (112), (211), (212), (301) and

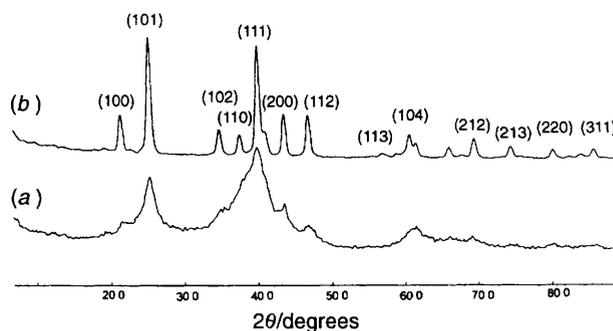


Fig. 4 X-Ray diffraction patterns of TaSi_x thin films deposited on Si(111) at 190 °C: (a) as-deposited; (b) after annealing

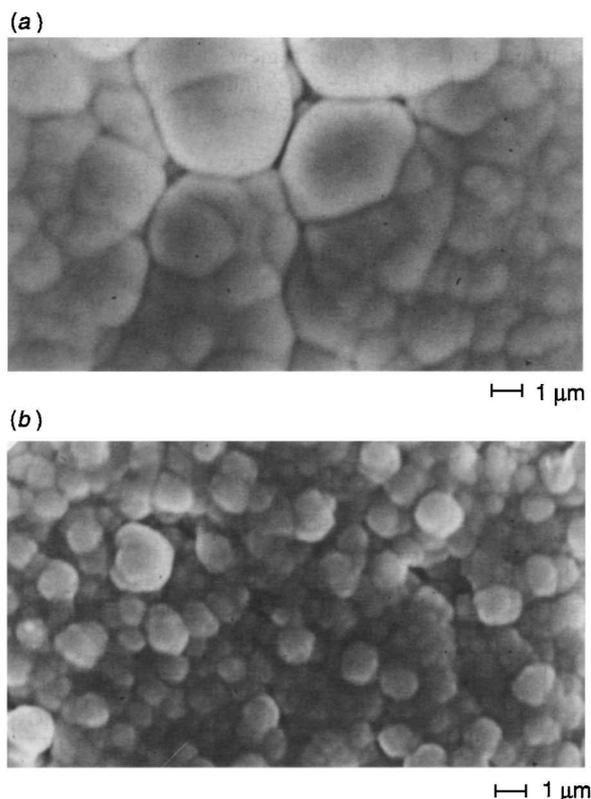
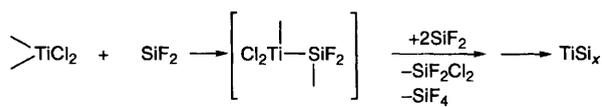
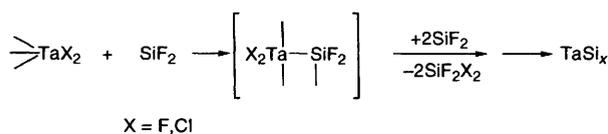


Fig. 3 SEM images of thin films on Si(111): (a) at 190 °C as-deposited; (b) at 300 °C as-deposited; (c) at 190 °C after annealing at 800 °C; (d) at 300 °C after annealing at 800 °C



Scheme 1



Scheme 2

(213) planes, respectively. Based on the diffraction patterns, the lattice parameters are estimated as $a=4.789$ and $c=6.573$ Å, which are slightly larger than the standard data. All these results suggest that the thin film was composed of 50% TaSi₂ and 50% a-Si.

The resistance of the thin films was found to be 35–50 μΩ, which is higher than the data reported for TaSi₂. This is attributed to the participation of 50% a-Si in the formation of the films.

In the deposition reaction of SiF₂ and TiCl₄,⁶ thin films of TiSi₂ were formed at 450–600 °C, with gaseous SiClF₃, SiCl₂F₂ and SiF₄ also produced. Based on these results, a reaction pathway for the formation of the TiSi₂ thin film is proposed as shown in Scheme 1. In this reaction, difluorosilylene acts both as a silicon source (the first step of the scheme) and as a halogen 'scavenger' (the second step). The observed gaseous products strongly support the second step of this reaction. On the other hand, there was no direct evidence for an intermediate involving the formation of Ti–Si bonds in the gas phase. In the reaction of TaCl₅ and SiF₂, the gaseous products were almost the same as those found for the TiCl₄ reaction, and a

similar reaction pathway is assumed. The *in situ* IR spectra of the reaction between SiF₂ and TaCl₅ in the gas phase showed characteristic bands of ν_{Si–F} (m; 840, 982 cm⁻¹) and ν_{Si–Cl} (m; 607 cm⁻¹). In the reaction of SiF₂ and TaF₅, the IR spectrum showed only a characteristic ν_{Si–F} band (m; 841, 990 cm⁻¹) and an absorption line at 522 cm⁻¹, which was assigned to Ta–F stretching vibrations. The blue shift of the ν_{Si–F} (from 840 and 982 to 841 and 990 cm⁻¹) caused by substituting TaF₅ for TaCl₅ can be interpreted in terms of the formation of a linkage between Ta and Si in the intermediate species. In parallel with the blue shift of the Si–F bond, the ν_{Ta–F} stretching vibration of TaF₅ (575 cm⁻¹) experienced a red shift (575 vs. 522 cm⁻¹) when TaF₅ reacted with SiF₂ in the gas phase. All these results suggest that some kind of linkage between Ta and Si was formed in the gas phase before deposition took place on the substrate of the hot-wall reactor. The TaSi_x film formation pathway is shown in Scheme 2.

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