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Difluorosilylene as a Precursor for the Chemical Vapour Deposition of Titanium Silicide

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A new method for preparing thin films of titanium silicide, $TiSi_2$, by chemical vapour deposition of difluorosilylene and titanium tetrachloride is reported.

Keywords: *Chemical vapour deposition; Titanium silicide; Thin film*

Transition-metal silicides have potential application in very large scale integrated circuits as metal–semiconductor interconnections and as low-resistivity gates because they are good conductors, they are chemically stable at high temperature and they are resistant to corrosion and degradation.[1] $TiSi_2$ has widespread application and interest because it has the lowest resistivity of the silicides.[2] Chemical vapour deposition is a good method of forming self-aligned titanium silicide films on silicon surfaces. Traditional methods involve the use of SiH_4 as the silicon source and $TiCl_4$ as the metal source at 700 °C.[3]

Difluorosilylene, SiF_2, is known to disproportionate to SiF_4 and Si at 650 °C.[4] We recently found that the best temperature range for Si deposition from SiF_2 was 350–400 °C.[5] The silicon films thus obtained were found to be amorphous by XRD. ESCA analysis showed a peak characteristic for silicon oxide in addition to the peak of silicon. The Auger electron spectroscopy depth profile showed that the oxygen content dropped below 1 atom% after 10 s of sputter time (E_p = 3 keV). The fluorine content was negligible throughout the profile. The IR spectrum also showed the complete absence of ν(Si—F) bands. This would suggest a new route to the synthesis of silicide thin films under milder conditions. We are particularly interested in systems where difluorosilylene and a co-precursor have a certain chemical interaction in the gas phase before deposition takes place. Titanium tetrachloride, was chosen as a co-precursor for titanium silicide films because it volatilizes readily and is known to react with SiF_2 in the gas phase.†

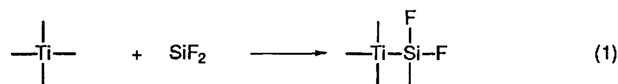
Chemical vapour deposition reaction of SiF_2 and $TiCl_4$ was carried out in a Pyrex vacuum system with the reaction zone being heated externally. Difluorosilylene was generated by the reaction of SiF_4 and Si at 1150 °C (with an approximate yield of 50%).[6] Difluorosilylene and the vapour of $TiCl_4$ were introduced into the system and thin films of $TiSi_2$ were formed on quartz, graphite and Si slides mounted in the heated zone (450–600 °C). The best ratio of partial pressure was found to be $p_{TiCl4}:p_{SiF4+SiF2} = 3:5$ (0.093 Torr : 0.156 Torr).‡

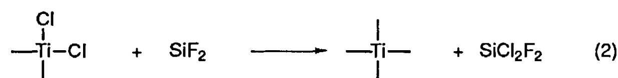
The film thickness can be controlled by deposition time and temperature. For example, films 2 μm in thickness can be prepared by using the partial pressures mentioned above over 2 h at 500 °C. The high purity of the crystalline $TiSi_2$ films was displayed by matching the XRD results with a standard. Both Auger electron spectroscopy (AES) and wavelength dispersion spectroscopy (WDS) showed the titanium and silicon in Ti:Si ratio of 1:2. The AES depth profile showed that the levels of O, C, Cl and F were negligible throughout the profile. Changes in total pressure in the range 0.105–0.046 Torr did not have any significant effect on the composition of the film. An analysis of the gaseous products by GC–MS revealed that in addition to an excess of SiF_4, $SiClF_3$ and $SiCl_2F_2$ were found in an approximate molar ratio of 4:1.

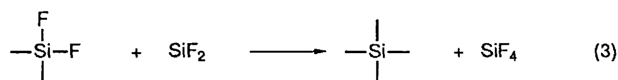
Using these results we may speculate a reaction pathway for the formation of the $TiSi_2$ film. The overall reaction can be written as follows:

$$TiCl_4 + 6\ SiF_2 \rightarrow 2\ SiClF_3 + SiCl_2F_2 + SiF_4 + TiSi_2$$

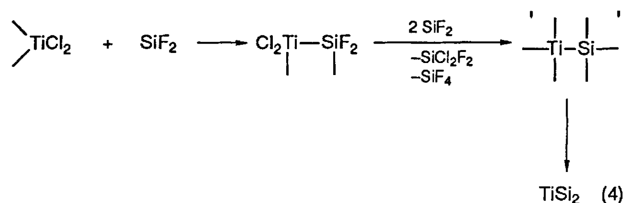
Note that in this case difluorosilylene acts both as a silicon source [eqn. (1)] and as a halogen 'scavenger' [eqn. (2) and (3)].







The combination of these two types of reaction results in a general reaction pathway which accounts for all the results observed experimentally.



In eqn. (4) difluorosilylene reacts with halides to generate SiF_4 and $SiCl_2F_2$, which forms $SiClF_3$ *via* halogen exchange:

$$SiCl_2F_2 + SiF_4 \rightarrow 2\ SiClF_3 \quad (5)$$

Obviously, other pathways cannot be ruled out at this time. The driving force of forming SiF_4 from SiF_2 that makes the deposition process clean and facile is remarkable.

It is likely that this type of reaction could be a generally

† The gas-phase reaction between $TiCl_4$ and SiF_2 yielded a dark purple solid, the analysis of which is underway.

‡ 1 Torr = (101325/760) Pa.

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useful one. We are currently exploring the scope of this method for the preparation of thin films of other metal silicides (with other volatile metal halides). For example, thin films of tantalum silicide and tungsten silicide have been prepared by reacting SiF_2 with $TaCl_5$ and WF_6 at 500 and 600 °C, respectively. The detailed analyses of these thin films are underway.

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