Thermal Deposition of TiS Films from Volatile Ti(SBu^t)$_4$

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Amorphous films of TiS are deposited by the low-pressure vapour-phase thermolysis of Ti(SBu^t)$_4$ at 130—200 °C.

The deposition of metal chalcogenides from the gas phase has so far involved the decomposition of two-component mixtures of volatile metal and chalcogenide compounds at high temperatures. For example, polycrystalline layers of TiS_2 are obtained by decomposing mixtures of $TiCl_4$ vapour and H_2S, either at 700—800 °C in a stream of argon carrier gas[1] or at 300—450 °C in a glow-discharge apparatus at low pressure,[2] and films of CdTe and ZnSe can be generated by the thermolysis of the respective metal dimethyls with dialkyltellurides or H_2Se.[3,4] Here we report the deposition of TiS films on glass supports *via* the gas-phase decomposition of the one-component precursor complex Ti(SBu^t)$_4$ under relatively mild conditions.

The complex Ti(SBu^t)$_4$ is accessible in almost quantitative yield from Ti(NMe$_2$)$_4$ and Bu^{t}SH as very air-sensitive deep-red crystals, which melt at 45 °C and begin to decompose at 70 °C. They are extremely soluble in non-polar solvents. The ^{1}H n.m.r. spectrum displays just one resonance at δ 1.68. The formation of a mononuclear thiolato complex in the case of titanium is in contrast with the analogous reaction of zirconium, *e.g.* Zr(CH$_2$Ph)$_4$ and Bu^{t}SH react to give Zr$_3$S(SBu^t)$_{10}$.[5]

When solid samples of Ti(SBu^t)$_4$ are heated under vacuum to 130 °C, the decomposing vapour of the complex deposits lustrous purple films on the reactor walls and on glass targets of the same temperature suspended above the sample. The films are transparent and *X*-ray amorphous. Scanning electron microscopy (SEM) reveals that the material is of homogeneous composition and non-crystalline, Figure 1; the titanium : sulphur ratio as determined by energy dispersive *X*-ray analysis varied from 1 : 0.98 to 1 : 1.02. Prolonged exposure to air leads to hydrolysis and formation of colourless films of TiO_2.

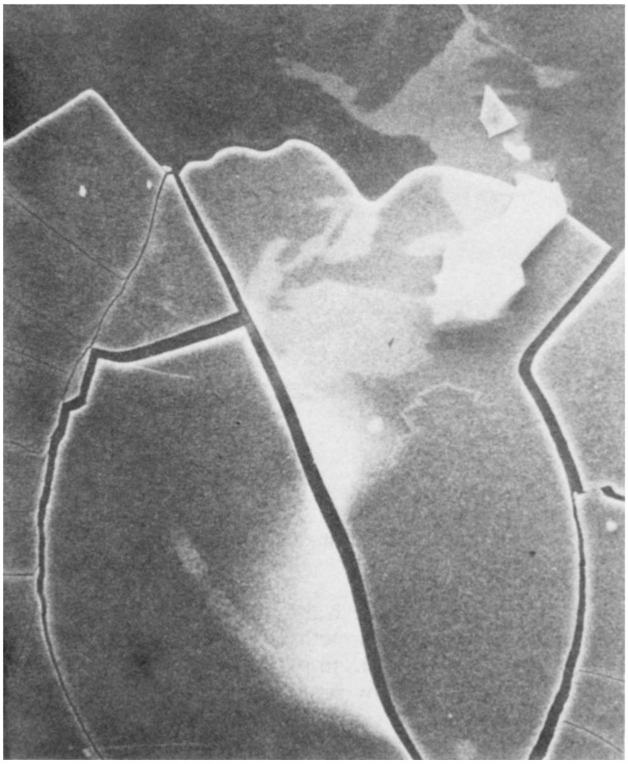

Figure 1. SEM image of a TiS film on glass. The fractures are caused by the impact of the electron beam; they show a random pattern which confirms the amorphous nature of the film. Deposition temperature 200 °C. Magnification ×190.

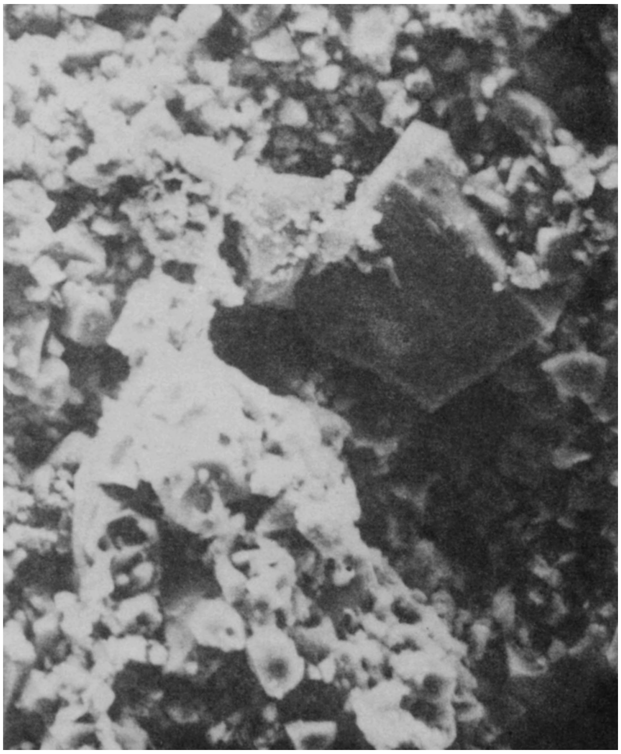

Figure 2. TiS powder produced by bulk thermolysis of $Ti(SBu^t)_4$ at 130 °C. Magnification ×540.

The bulk decomposition of crystalline $Ti(SBu^t)_4$ gives rise to an insoluble black solid which shows similar Ti : S ratios. Material obtained at 130—200 °C contains *ca.* 5% carbon; this is reduced to 3% on heating to 415 °C for 6 h.† Although powdered samples exhibit a crystal-like habit on the SEM image, Figure 2, they too do not produce *X*-ray diffraction patterns, even after prolonged tempering at 415 °C.‡

The thermal decomposition of $Ti(SBu^t)_4$ to TiS involves a reduction of titanium, as expressed by equation (1). The formation of Bu^t_2S and $Bu^t_2S_2$ in about equal amounts was verified by the g.c.–m.s. analysis of the organic products trapped at low temperatures; a small amount of butane was also detected. By contrast, the recently reported bulk decomposition of the polymeric methyl thiolates $[M(SMe)_2]_n$ (M = Zn,Cd) gives Me_2S as the only identifiable organic product.[7]

$$Ti(SBu^t)_4 \rightarrow TiS + Bu^t_2S + Bu^t_2S_2 \qquad (1)$$

The results show that the gas-phase deposition of metal sulphide films can be achieved under mild conditions using preformed thiolato complexes as one-component precursors, provided the steric requirement of the thiolato ligands is sufficient to prevent higher degrees of metal association and loss of volatility.

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References

1 S. Motojima, K. Itoh, Y. Takahashi, and K. Sugiyama, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3240.

2 R. Shimanouchi, T. Yamamoto, S. Kikkawa, and M. Koizumi, *Chem. Lett.*, 1985, 1323.

3 W. K. Hoke and P. J. Lemonias, *Appl. Phys. Lett.*, 1986, **48**, 1669.

4 J. I. Davies, G. Fan, M. J. Parrott, and J. O. Williams, *J. Chem. Soc., Chem. Commun.*, 1986, 68.

5 D. Coucouvanis, A. Hadjikyriacou, and M. G. Kanatsidis, *J. Chem. Soc., Chem. Commun.*, 1985, 1224.

6 H. Hahn and B. Harder, *Z. Anorg. Allg. Chem.*, 1956, **288**, 16.

7 K. Osakada and T. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 1987, 1117.

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† The volatile material given off under these conditions includes C_2H_4, H_2S, MeSH, Me_2S, and traces of MeSEt.

‡ Crystalline TiS can be prepared from the elements in two modifications at 700 and 1000 °C, respectively; the structure is of the NiAs type.[6]