A two-step low pressure chemical vapour deposition process for the production of tungsten metal thin films

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A two-step process for the production of $W_{(m)}$ thin films on Si(100) and SiO_2/Si(100) is described involving the initial low pressure chemical vapour deposition of tungsten carbide from $(Bu^tCH_2)_3W{\equiv}CBu^t$ at 350 °C followed by a post-treatment with H_2 (500–700 °C) or H_2 plasma at 350–700 °C.

Metal films find several industrial applications because of their refractory characteristics. Also applications from wear and corrosion protection to conducting layers and diffusion barriers in electronic devices are of importance. For the latter, the metals of primary interest are W, Al, Cu, Pd, Pt, Au and Ti.[1] The CVD of both $Al_{(m)}$ and $Cu_{(m)}$ have received much attention and a considerable knowledge of the chemistry involved in depositing these metals is now available. Among other things this has allowed the use of surface modification in order to obtain selectivity in deposition.[2] Of the metals noted above tungsten offers certain distinct advantages with respect to its inertness in contact with all major III–V semiconductors even at high temperatures and prolonged contact times.[3] Traditional routes to tungsten films involve reactions between WF_6 and H_2 or SiH_4.[4] These methods are not environmentally friendly because they lead to the formation of the noxious gases, HF and SiF_4. In addition, silane and WF_6 are themselves extremely reactive and require elaborate safety procedures. We describe here the first report of the production of tungsten films by a two-step low pressure chemical vapour deposition (LPCVD) process involving the use a metalloorganic precursor, $(Bu^tCH_2)_3W{\equiv}CBu^t$.

$(Bu^tCH_2)_3W{\equiv}CBu^t$ was prepared by the reacton between $(Bu^tO)_3W{\equiv}CBu^t$ and excess Bu^tCH_2MgCl in diethyl ether.[5] Low-pressure chemical vapour depositions were carried out with a simple hot-walled reactor. The substrates chosen for this study are p-type Si(100) and SiO_2/p-type Si(100) wafers. They were washed with isopropyl alcohol and light petroleum (bp 60 °C) and rinsed with distilled water (in the case of the Si wafers, HF was used) and were stored in isopropyl alcohol. The substrates were placed at the center of the hot zone (350 °C). In the first step, the precursor was transported at 55 ± 2 °C under vacuum to the deposition chamber.[5,6] Highly reflective and smooth tungsten carbide films formed on the substrates and on the wall of the hot chamber. In the second step, the amorphous tungsten carbide films were treated with H_2 (500–700 °C) or H_2 plasma in the temperature range 350–700 °C, for 2 h [eqn. (1)].

$$(Bu^tCH_2)_3W{\equiv}CBu^t \xrightarrow[\text{LPCVD}]{350\ °C} \text{Tungsten carbide} \xrightarrow[H_2 \text{ or } H_2 \text{ plasma}]{500\text{–}700\ °C} W_{(m)} \quad (1)$$

The H_2 plasma was inductively coupled at 13.5 MHz with a power density on the order of 5 W cm^{-2}.

The thin films produced after this post-deposition annealing were studied by XRD, XPS, Auger, SEM and four-point sheet resistance probes. Annealing at temperatures below 500 °C leaves amorphous films [broad XRD band centered near 39° (Cu-Kα radiation)]. Annealing at temperatures above 500 °C in an H_2 plasma produced crystalline α-W X-ray patterns but SEM revealed a rough and pitted surface morphology for these films. Films annealed in an H_2 atmosphere retained the high density and surface morphology of the original tungsten carbide films but did not produce pure α-W X-ray patterns at temperatures below 600 °C within 2 h. The XRD of a $W_{(m)}$ film on Si(100) prepared at 700 °C is shown in Fig. 1.

The chemical purity of the films was estimated by Auger spectroscopy (with depth profiling) and XPS. Figs. 2 and 3

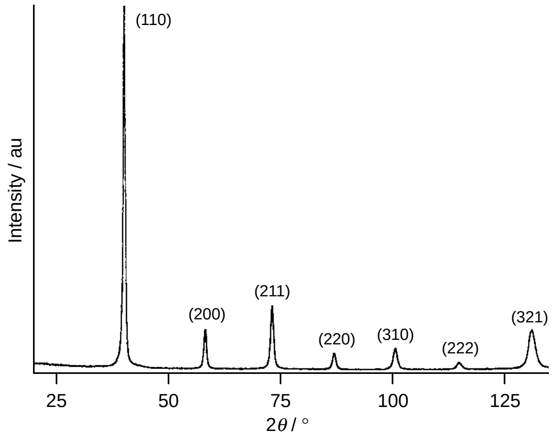

Fig. 1 X-Ray diffraction (Cu-Kα radiation) spectra of W metal film on SiO_2/Si(100) after post processing under H_2, flowing at 10 sccm, at 973 K for 2 h

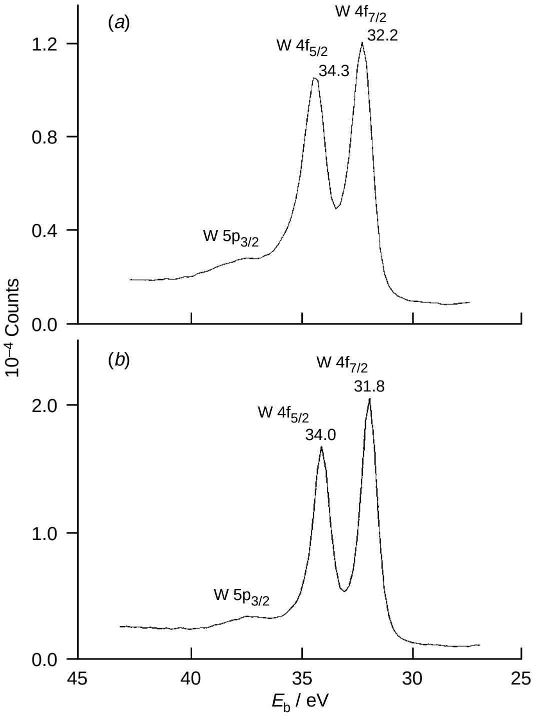

Fig. 2 (*a*) XPS spectra on W 4f region of the tungsten carbide film deposited on Si(100) under vacuum at 623 K for 2 h by $(Bu^tCH_2)_3W{\equiv}CBu^t$. (*b*) XPS spectra on the W 4f region of the tungsten metal film on Si(100) produced after post-treatment with H_2, flowing at 10 sccm, at 973 K for 2 h.

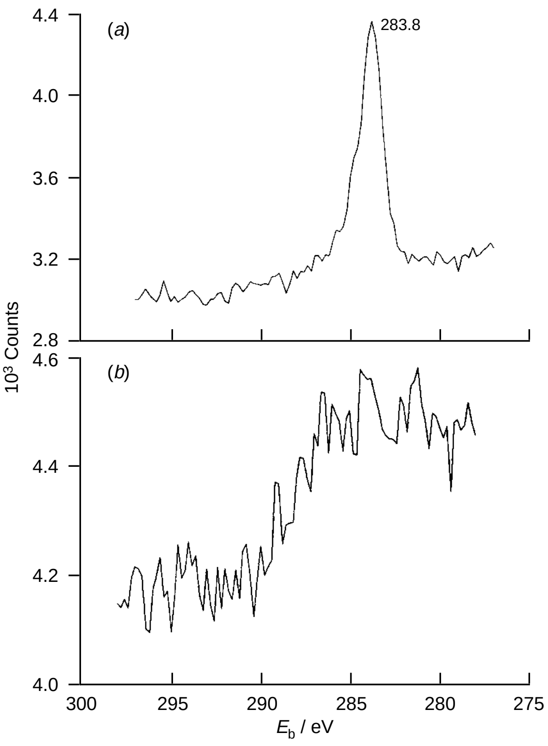

Fig. 3 (*a*) XPS spectra on the C 1s region of tungsten carbide film deposited on Si(100) under vacuum at 623 K for 2 h by $(Bu^tCH_2)_3W{\equiv}CBu^t$. (*b*) XPS spectra on the C 1s region of the tungsten metal film on Si(100) produced after post-treatment with H_2, flowing at 10 sccm, at 973 K for 2 h.

show the XPS data collected near the W 4f and C 1s energies for WC films as originally deposited and after 700 °C, H_2 annealing. These figures demonstrate a carbon content below the detection limit (*ca.* 2%) for this method.

The resistivities for all the films were > 50 μΩ m, a value too large to be of direct interest for integrated circuit metallization. At least for the plasma annealed films this large resistivity could reflect the poor morphology noted above. It may be that a more gentle remote plasma treatment could produce more conductive films while still removing the carbon impurities. However, the resisitivity of our films of $W_{(m)}$ compare favorably with others produced by CVD.[7]

It should be noted that this two-step process for the production of $W_{(m)}$ films avoids the problems of high carbon content contamination that a one-step process entails when using an organometallic such as $W(CO)_6$, $W(\eta\text{-}C_6H_6)_2$, Cp_2WH_2 or $W(allyl)_4$ in the presence of an H_2 carrier gas.[1d] Indeed, in our studies we find that attempts to prepare $W_{(m)}$ from $(Bu^tCH_2)_3W{\equiv}CBu^t$ by LPCVD in the presence of H_2 results in carbonaceous films.

To conclude, we have discovered a new route for the formation of $W_{(m)}$ films by a two-step LPCVD process. The two step process may be compared with the industrially significant process employing $Ti(NMe_2)_4$ in the synthesis of TiN,[8] wherein Ti(C,N) is first formed by CVD and then in a post treatment with NH_3, converted to pure TiN. The potential advantage of the use of a volatile organometallic tungsten precursor clearly lies in the avoidance of noxious substances such as SiH_4, HF and WF_6. Other organotungsten compounds can be used to prepare tungsten carbide films[9] so one is not limited to the volatile liquid precursor $(Bu^tCH_2)_3W{\equiv}CBu^t$, though this precursor does offer the advantage of minimizing graphite content in the films. Also the present procedure does not require the use of ultrahigh vacuum procedures as has been claimed in the synthesis of $W_{(m)}$ from $W(CO)_6$ at 540 °C.[10] Further investigations of this approach seem justified.

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Notes and References

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