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Deposition and Characterization of CVD–Tungsten and Tungsten Carbonitrides on (100) Si

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Abstract: Two different precursors were used to deposit W films on Si–$W(CO)_6$ and WCl_6. By pyrolytic decomposition of $W(CO)_6$ at 400°C in argon atmosphere W thin films with well-expressed textured structure were deposited on (100)Si substrates. By hydrogen reduction of WCl_6 at 750°C in Ar, polycrystalline W films were deposited. By the carbonyl process and in the presence of ammonia and acetone, WC_xN_y thin films were obtained. Reflection High Energy Electron Diffraction (RHEED) method was used for structural characterization of the films. Temperature dependence of the electrical resistance of the films in the range 4·2–300 K was studied and the results are discussed in terms of films structure and composition.

1 INTRODUCTION

Thin films of tungsten and its compounds were studied in different aspects, including application in solar energy conversion as black metals solar selective surfaces[1,2] and as electrochromic materials.[3] For the purposes of IC metallization many authors have investigated CVD W and its interaction with other thin film surfaces.[4] The fluoride CVD W technology often leads to problems because of the aggressive fluorine which attacks the thin film surfaces forming interlayers which influence contact resistance and stability of the interconnection. It is of interest to investigate W films obtained by an alternative to the fluoride technology route.[5] Besides, the CVD method is now popular not only in the preparation of thin films for microelectronics but for wear-resistant hard coatings.

The aim of the present paper is to compare W thin films deposited on Si(100) substrates by CVD of $W(CO)_6$ and WCl_6 precursors and WC_xN_y films deposited at low temperatures by CVD of $W(CO)_6$ in presence of ammonia and acetone.

2 EXPERIMENTAL TECHNIQUES AND MATERIALS

The CVD equipment used a quartz reactor with inductively heated graphite susceptor. The temperature was controlled by a Pt/Pt.Rh thermocouple connected with thermoregulator, switching on and off one of the phases of the high frequency generator. The substrate temperature was controlled with an accuracy of ± 10°C. The source material was placed in a sublimator immersed in a silicone oil bath. The temperature of the sublimator was controlled with an accuracy of ± 1°C. $W(CO)_6$ or WCl_6 precursors were heated at 100°C or 140°C, respectively. The vapours are carried by an argon flow, which enters the CVD reactor. The susceptor with silicon substrates was heated up to 400°C in the case of the carbonyl process and up to 750°C in the case of the chloride process. Films of WC_xN_y were obtained by *in-situ* CVD carbonyl process with addition of ammonia and acetone. The following reactions are expected to take place:

$$W(CO)_6 \xrightarrow[Ar]{400°C} W + 6\,CO$$

$$WCl_6 + 3H_2 \xrightarrow{750°C} W + 6HCl$$

$$W(CO)_6 \xrightarrow[NH_3 + CH_3COCH_3]{400°C} WC_x N_y$$

High-purity gases were used in the experiments: 99·95 % and 99·995% for argon and hydrogen, respectively. The ammonia and acetone used were of purity for microelectronics purposes. The argon and hydrogen passed through a drying system.

The Reflection High Energy Electron Diffraction method, X-ray microprobe analysis and Auger electron spectroscopy were used for structural and compositional characterization. Film resistivity was measured by an FPP 300 electronic device.

3 RESULTS AND DISCUSSION

3.1 Structure characterization

Thin W films were deposited on (100)Si substrates by pyrolytic decomposition of $W(CO)_6$ at 400°C and atmospheric pressure. Structural studies of as-deposited films show that they grow textured. The RHEED diffraction pattern is shown in Fig. 1. It is known from previous studies[2] that as-deposited carbonyl W films contain considerable amounts of carbon and oxygen. Texturing of the film is unexpected having in mind the impurities in the film. The lattice parameters of (100) Si (5·431 Å) and β-W (5·036 Å) are 8% off. This makes an 'expitaxial' relation highly unlikely. The reason for the observed texture one can suppose to be the nature of the carbonyl CVD process. Similar investigations for Mo films obtained on polycrystalline substrates by pyrolytic decomposition of $Mo(CO)_6$ have shown texturing in different crystallographic directions.[6] Sivaram notes that W films deposited by silane reduction of WF_6 are textured along the (110) direction when deposited on TiN, in spite of the 34% lattice mismatch between TiN and W.[7] These observations point in the direction that it is not the lattices' relation which gives the texture. More probable are differences in growth rate for the various crystal planes.

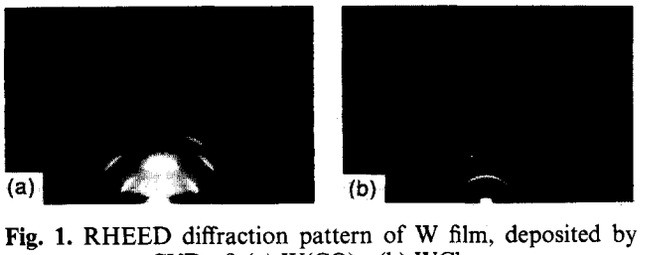

Fig. 1. RHEED diffraction pattern of W film, deposited by CVD of: (a) $W(CO)_6$; (b) WCl_6.

Thin films of W on (100)Si were deposited by hydrogen reduction of WCl_6 at atmospheric pressure. The structure of the films was investigated by RHEED and the observations showed b.c.c. polycrystalline structure — see Fig. 1(b). The observed *d*-spacings (2·28, 1·61, 1·31 and 1·12 Å) coincide well with the expected (2·23, 1·58, 1·29 and 1·11 Å) ones. It is seen from the RHEED diffraction pattern on Fig. 1(b), that CVD chloride W films do not grow textured.

RHEED investigation of WC_xN_y films shows that these films have a polycrystalline structure, consisting of small grains. Diffraction pattern was weak and texture was not observed. We refer to some of our recent studies which show that these small-grained, polycrystalline WC_xN_y films are the best diffusion barriers for cobalt. No cobalt was registered by X-ray microprobe analyses of WC_xN_y when deposited on a cutting tool, containing about 8% cobalt.

3.2 Electrical resistance measurements

Resistance vs temperature dependence of the investigated samples was measured in the range 4·2–300 K by four-point probe method. A platinum thin film calibrated thermometer was used in the experiment. The resistance at room temperature of the investigated samples is presented in Table 1.

The temperature dependence of the resistance *R* vs *T* of W films on Si(100) is presented in Fig. 2. W film obtained from the carbonyl precursor (sample A) possesses lower room-temperature resistivity which remains constant with decrease of temperature, while the W film obtained from the chloride precursor (sample B) shows typical metallic behaviour.

The reason for the unchanged resistance is possibly the chemical impurities (carbon and oxygen) resulting from the carbonyl decomposition. However, additional rapid thermal annealing at 600–

Table 1. Processing procedure and room-temperature resistance of W and WC_xN_y films

Sample	Processing procedure	Resistance ρ (300 K) [μΩ.cm]
A	W by carbonyl precursor	108·8
B	W by chloride precursor	122·4
C	*In-situ* CVD WC_xN_y	651·1

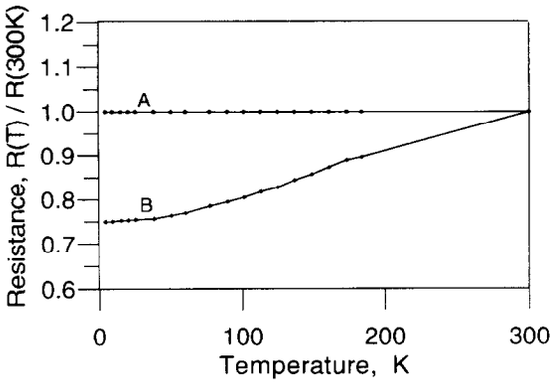

Fig. 2. Resistivity $R(T)/R_{300K}$ vs temperature T of W-CVD films obtained by: (A) pyrolytic decomposition of $W(CO)_6$; (B) hydrogen reduction of WCl_6.

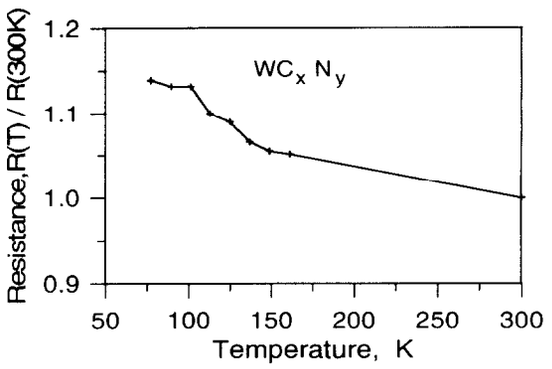

Fig. 3. Temperature dependence of the electrical resistance of WC_xN_y film, deposited by CVD of $W(CO)_6$ in presence of acetone and ammonia gases.

1200°C as well as longer-term treatment with hydrogen were shown to lead to significant decrease of room-temperature resistivity. By annealing, resistivities of 17 $\mu\Omega$.cm for the carbonyl W films have been achieved.[5] The significant decrease of the resistivity is possibly due to the removal of carbon and oxygen impurities at the grain boundaries and to phase transformations appearing at high temperatures.

In Fig. 3 the temperature dependence of the electrical resistance of WC_xN_y films is presented for the range of temperatures 77–300 K. The room-temperature resistivity is 651 $\mu\Omega$.cm (sample C in Table 1) and its slow decrease with increasing temperature is clear. The carbides and nitrides of the transition metals are known as hard-metal materials, exhibiting semimetal properties.

4 CONCLUSIONS

Two kinds of W film which differ in their structures and electrical properties were studied. Tungsten films deposited by CVD of $W(CO)_6$ grow textured, they are low resistive and maintain their electrical resistance unchanged over a broad temperature range. Tungsten films deposited by CVD of WCl_6 have typical metal behaviour. WC_xN_y films, deposited by CVD of $W(CO)_6$ in presence of ammonia and acetone show semiconductor behaviour; their electrical resistance decreases with increasing temperature. W films, as well as WC_xN_y films obtained by low-temperature CVD technology, are prospective materials for different applications.

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