

R.F. magnetron sputtered tungsten carbide thin films

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Abstract. Thin films of tungsten carbide have been deposited on stainless steel substrates held at 500°C by r.f. reactive magnetron sputtering in two different modes of introducing argon and acetylene gases called normal and high rate mode. A single phase fcc-WC is formed in the normal mode whereas a mixture of A-15-W₃C, hexagonal-WC and graphitic- and diamond-carbon is found in the high rate mode. A microhardness value as high as 3200 kgf/mm² (as compared to the bulk value of 1800 kgf/mm²) is obtained in the film deposited by normal mode.

Keywords. Tungsten carbide; magnetron sputtering

1. Introduction

High rate reactive magnetron sputtering process for thin film deposition is important for industrial applications. Several workers (Aronson *et al* 1980; Schiller *et al* 1984; Kaiza *et al* 1981) have developed such techniques to deposit thin films of various transition metal carbides, nitrides, oxides etc for wear-resistant and protective coatings on various substrates like cemented carbide tools, high speed steel, copper and copper alloys. Efforts to enhance the deposition rate by effective control of the flow of reactive gases into sputtering chamber have been made. The processes that occur on the magnetron target surface are dependent on the interaction between sputter products and reactive gaseous products as well as on the degree of coverage of the reaction products obtained on the target. Generally in reactive sputtering, the target metal gets carburized, nitrated or oxidized by the reactive gases and subsequently sputtered at low rates since the sputtering yield for carbides, nitrides or oxides is much lower than those of the corresponding metals. Schiller *et al* (1980) deposited various compounds with very high rates by using a dc magnetron-plasmatron system in such a way that practically complete separation of solid component sputtering at the target and of the reaction of the produced particles with the gaseous component during condensation occurs on the substrate. They were able to sputter various compounds with very high rate ($\sim 1 \mu\text{m}/\text{min}$ for Ta₂O₅). Recently Scherer and Wirz (1984) used a similar configuration for sputtering of Al₂O₃.

We have prepared tungsten carbide films by reactive r.f. magnetron sputtering on stainless steel substrates. The substrate temperature, flow of gases and bias potential of the cathode were controlled to obtain hard adherent coatings. Two different modes of introducing argon and acetylene gases were studied. In one, called the normal mode (NM), the two gases were homogeneously mixed in the plasma region whereas in the other, called the high rate mode (HRM), separate zones of argon and acetylene were created by controlling the flow of the two gases such that the carbide formation on the

tungsten target could be reduced (Srivastava *et al* 1985). The WC_x films formed in both the modes were analyzed by x-ray diffraction (XRD) and Auger electron spectroscopy (AES) for their structure and compositional analysis. The microhardness was measured by Vicker's microhardness tester fitted onto Carl Zeiss optical microscope. The indents produced during the microhardness measurements were also analyzed in a scanning electron microscope (SEM).

2. Experimental details

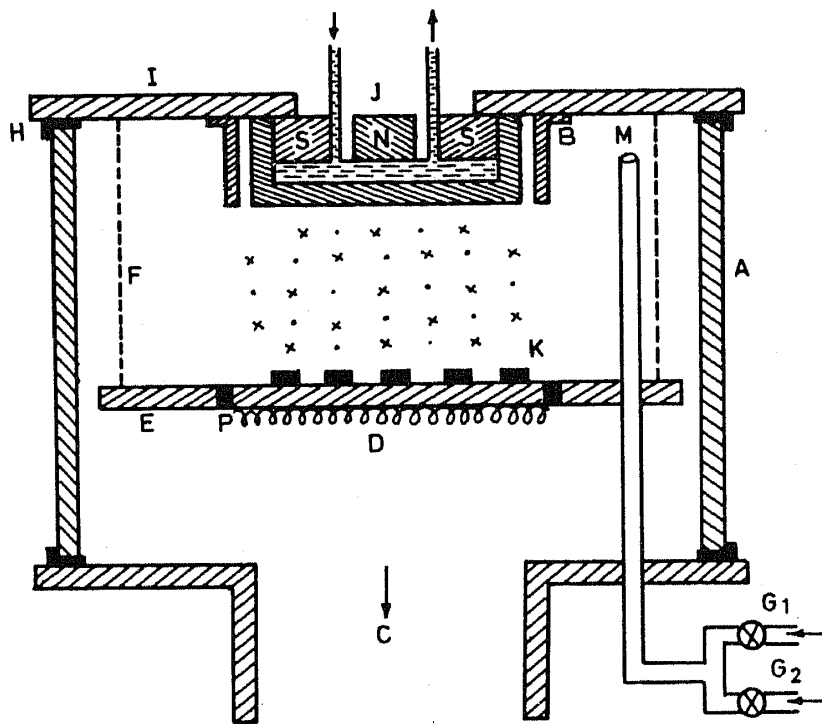
Figure 1 shows the magnetron sputtering system used for deposition of tungsten carbide films on stainless steel substrates held at 500°C in the normal mode (a) and in the high rate mode (b). Preparation of substrates for deposition and various conditions for sputtering is reported elsewhere (Srivastava *et al* 1984). Flow rates of argon and acetylene gases were maintained at 30 scc/min and 6 scc/min, respectively for both systems. An r.f. power density of 4.5 watt/cm² was maintained during sputtering. This developed a target bias voltage of 500 volts. For each run, the substrate temperature, flow of gases and the bias potential developed on the cathode were kept constant. Under similar conditions the deposition rate of tungsten films and tungsten carbide films in normal and high rate mode are 825, 600 and 825 Å/min respectively.

An x-ray diffractometer (Philips PW 1730/10) was used for x-ray analysis in $\theta - 2\theta$ scan mode using CuK_{α} (1.54 Å) radiation and 1°/min scan speed. For compositional analysis, a scanning Auger microprobe (PH1 590) with electron beam of 0.2 µm diameter was used. The sputter depth profile was performed with an ion gun of ~200 µm diameter operated at 5 kV and current density 600 µA/cm².

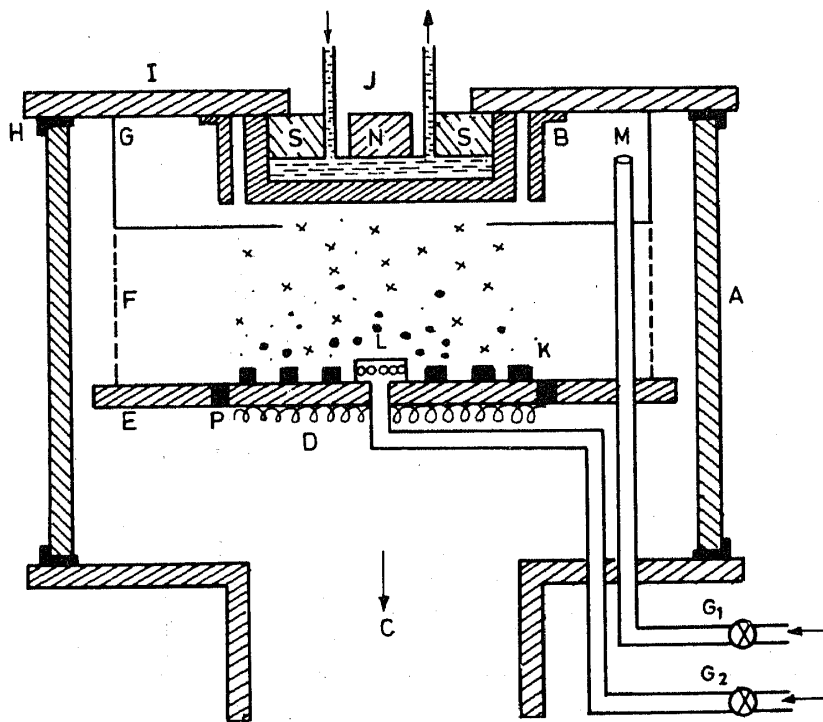
3. Results and discussion

Figure 2 shows the XRD profiles for 4.2 µm thick films deposited at 500°C in the normal mode (a) and in the high rate mode (b). The maximum grain size as calculated from the broadening of x-ray peaks is ~300 Å for both types of films. Since at different temperatures the structure and composition of the film are different, correlation of the grain size variation with temperature is not possible. The interplanar spacings d were calculated from the XRD and compared with standard data (ASTM data cards). The NM films deposited at 500°C on stainless steel are cubic tungsten monocarbide (f.c.c. B1 structure) while the HRM films deposited at 500°C are a mixture of various phases, namely A-15 W_3C , hexagonal WC, graphitic carbon and diamond carbon.

Figure (3a) shows the AES traces of the surface of WC_x films which is a typical feature of all the films sputtered in both modes. Oxygen ($KL_{2,3}L_{2,3}$ -512 eV) is a major impurity on the surface. The presence of carbon is indicated by a peak ($KL_{2,3}L_{2,3}$ -271 eV) which has a characteristic shape suggesting the formation of graphitic phase on the surface. Inside the bulk of the NM film the shape of this peak changes and additional features at 252 eV and 260 eV appear (figure 3b). Such features are characteristic of carbide phase formation (Moyoshi and Buckley 1982). Similar peaks at 252 eV and 260 eV appear in the HRM films but these peaks are not very sharp suggesting that the carbide phase formation is not complete and a mixture of graphitic and carbidic phases are present (figure 3c). Thus XRD and AES profiles are found consistent with each other. AES



(a)



(b)

Figure 1. Schematic diagram of reactive r.f. magnetron system in (a) normal mode, (b) high rate mode showing metallic belljar (A), target shield (B), vacuum pump (C), substrate heater (D), grounded base plate (E), perforated aluminium mesh (F), aluminium metallic partition (G), L gasket for vacuum sealing (H), top plate (I), target (J), substrate (K), opening of reactive gas (L), opening of inert gas (M), insulator ring (P), and precision needle valves (G_1 and G_2).

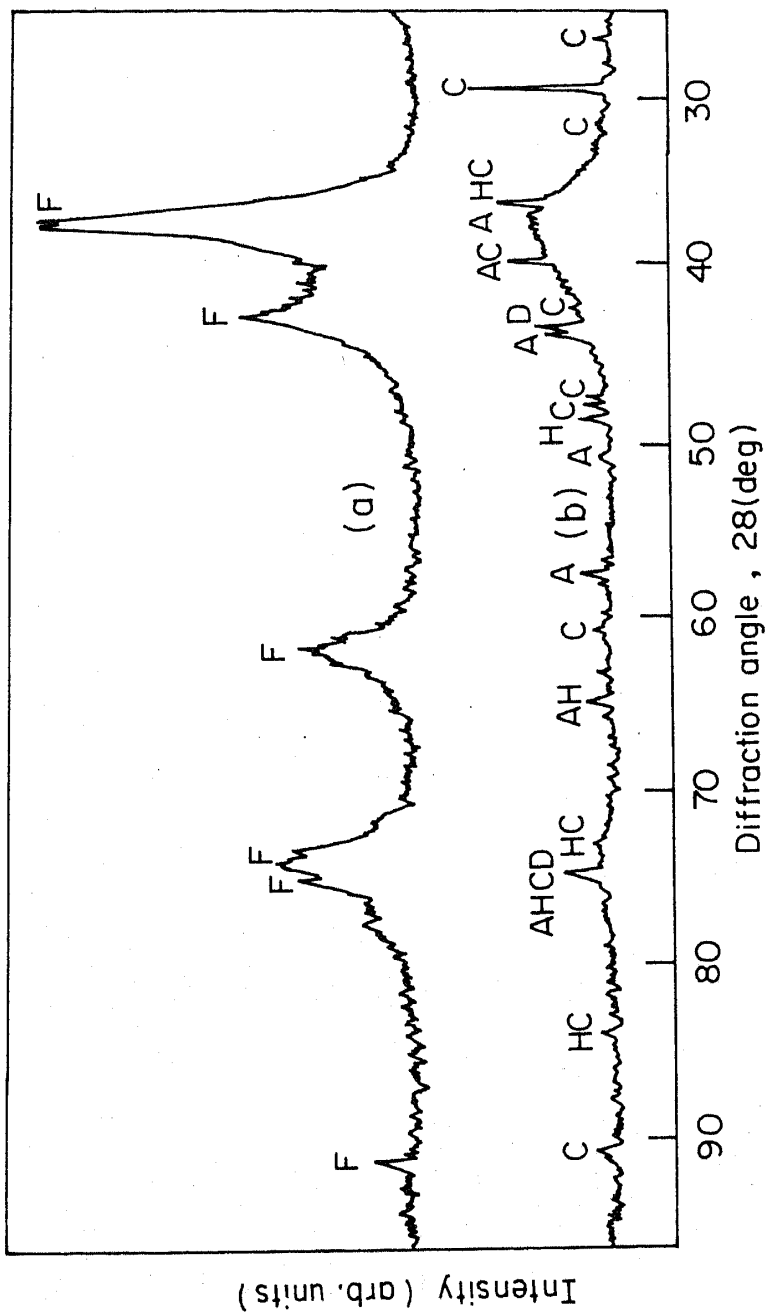


Figure 2. X-ray diffraction profiles of WC_x films prepared on stainless steel substrates at $500^\circ C$ in (a) normal mode, (b) high rate mode showing A-15 W_3C phase (A), hexagonal WC phase (H), graphitic carbon (C) and diamond carbon phase (D), and fcc WC_x phase (F).

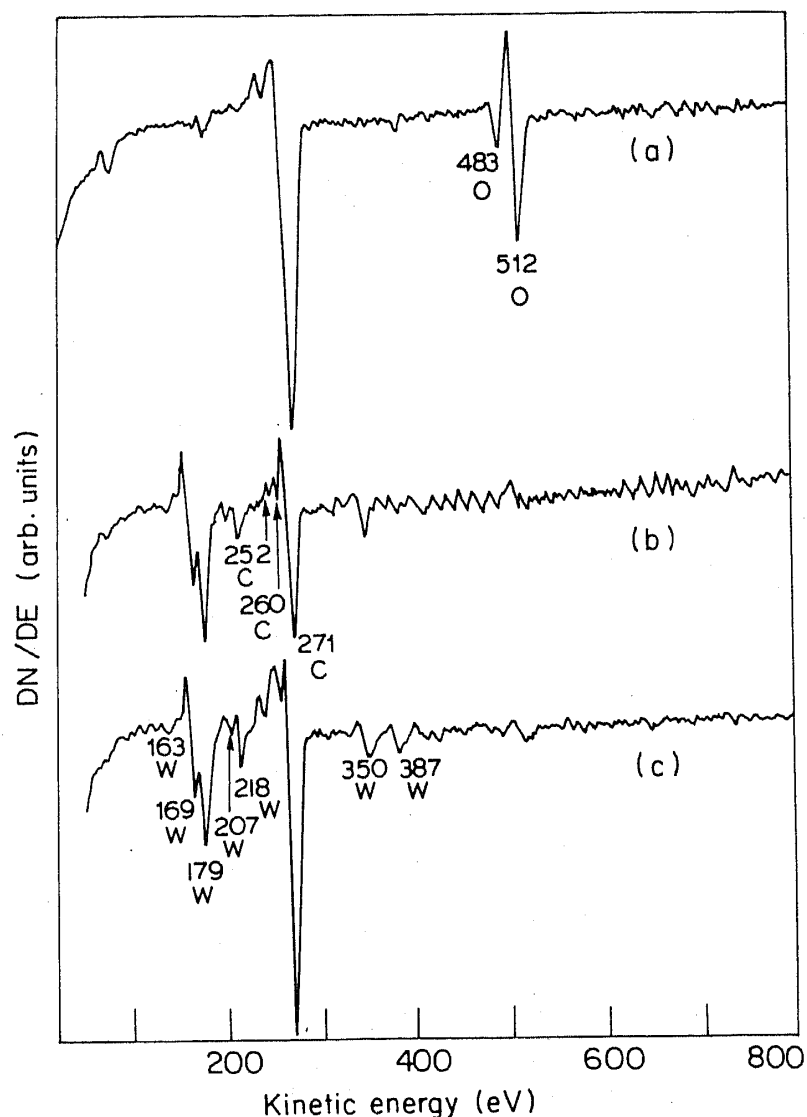


Figure 3. AES profile of WC_x films deposited at 500°C on stainless steel substrate at (a) and surface of HRM films, (b) 100 Å depth from the surface of NM films, and (c) 100 Å depth from the surface of HRM films.

analysis yields the composition of these films as 50% W, 50% C for NM films, and 40% W, 60% C for HRM films.

The microhardness of the films has been measured by Vicker's microhardness indenter and value of 3200 and 2365 kgf/mm^2 is observed at 10 g load for NM and HRM films respectively. It should be noted that the bulk hardness of tungsten carbide (hexagonal phase) is 1800 kgf/mm^2 . The higher values observed in NM films may be due to fine grain size and B1 fcc crystal structure. HRM films crack during the microhardness measurement and a circular crack pattern is developed around the indentation. The number of the circles increases with increasing load and three concentric circles are formed at a load of 160 g. In the case of NM films such cracks around the indentation are not observed.

The XRD and AES studies suggest that the HRM films have excess free carbon in graphitic and diamond form which is dispersed in W_3C (A-15 phase) and WC (hexagonal

phase) resulting in brittle films (as observed in microhardness measurements) which develop cracks at higher loads. On the other hand, NM films have single phase and are less brittle and, therefore, do not crack at loads as high as 160 g.

4. Conclusions

- (i) Rates of deposition of WC_x films as high as that of pure tungsten have been achieved by dividing the inert and reactive gases in separate zones and controlling their flow patterns in such a way that the carbide formation on target surface is avoided.
- (ii) W_3C (A-15 phase), WC (hexagonal) and carbon (graphitic and diamond form) are obtained in the films prepared in the modified geometry whereas in the normal geometry a single phase fcc tungsten monocarbide is formed.
- (iii) A microhardness value as high as 3200 kgf/mm^2 at 10 g load has been obtained in single phase fcc WC_x films whereas the films containing a mixture of phases and dispersed carbon have lower microhardness (2365 kgf/mm^2) at 10 g load.

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