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Tungsten–carbon thin films deposited using screen grid technique in an electron cyclotron resonance chemical vapour deposition system

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Abstract

A new technique for depositing metal–carbon(Me–C:H) thin films is proposed based on two metal screen grids embedded within an electron cyclotron resonance chemical vapour deposition(ECR–CVD) system. The grids are negatively biased and supported at adjustable distances above the substrate holder in the deposition chamber. With source gases of methane and argon, sputtering of the metal grids by Ar^+ results in the incorporation of metal in the growing carbon films. The amount of metal in the films can be very well controlled over a wide range by varying the bias voltage of the grids, the separation of the grids from the substrate holder and the ratio of CH_4/Ar. Furthermore, by separately biasing the substrate holder, the properties of the films can be varied resulting in the formation of a great variety of Me–C:H films with very different mechanical and structural properties. Tungsten incorporated carbon films(W–C:H) were deposited using this technique with two tungsten (W) grids biased at −330 V. The fraction of W in the films was controlled by varying the flow ratio of CH_4/Ar. The films were characterized using Rutherford backscattering and X-ray photoelectron spectroscopy measurements, and also in terms of their conductivity, optical absorption and hardness. The conductivity was found to increase by six orders of magnitude whereas the optical gap decreased by 1.5 eV with an increasing atomic fraction of W in the films from 2% to 8%. WC bonds were not detected, and the W detected was mainly in the form of WO_2 and WO_3. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Diamond-like carbon; ECR–CVD; Metal–carbon films

1. Introduction

Metal incorporated carbon (Me–C:H) films with properties intermediate between diamond-like carbon (DLC) and metal carbides have been shown to have small frictional values, extremely low abrasive wear rates and good adhesion to metal substrates [1,2]. Furthermore, the conductivity of these films can be varied over many orders of magnitude and the conduction behavior ranges from that of semiconductor to metallic-like depending on the metal content [2]. Several techniques have been proposed for the deposition of Me–C:H films, which include sputter deposition in a hydrocarbon and Ar gas mixture [3], rf magnetron sputtering [4], plasma polymerization of a volatile metal organic compound [5], energetic metal ion implantation [6], co-evaporation of polymer and metal [7], co-sputtering of polymer and metal [8], and recently by magnetron assisted pulsed laser deposition [9]. A variety of different Me–C:H films have been studied, the more common metals incorporated include Ta, Ti, Fe and W [3–6,9]. The investigations have so far focused on the tribological properties of the films in terms of their applications as hard and low frictional coatings, and also on the microstructures of the films, such as the chemical state of the metal in the films and whether it segregates into clusters or forms nanocrystalline carbides in an a–C:H matrix. Other characteristics such as optical properties and electrical conductivities have also been investigated, but to a lesser extent [2]. Metals that do not form carbides, such as Au, Ag and Cu, have also been studied to shed light on the characteristics of these films having metal clusters embedded in an insulating host [2,8,10].

The different deposition processes have their advan-

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tages and limitations. In terms of limitation, specifically, in sputtering process the sputtering of the target and the ionization of the source gases cannot be independently controlled, and poisoning of the target sets a lower limit (2%) on the fraction of metal that can be incorporated [11]. Plasma polymerization of a volatile metal organic compound is naturally limited to the types of accessible compounds, and there is also very limited control of the metal fraction in the films as it was found to be determined mainly by the Me:C atomic ratio of the precusors [5].

In the present work, we report on a new technique for depositing Me–C:H films using an electron cyclotron resonance chemical vapour deposition (ECR–CVD) system in conjunction with a metal screen grid fixture situated within the deposition chamber. This screen grid technique was previously developed for the deposition of DLC under direct dc bias in an ECR–CVD system [12]. Besides the unique characteristic of having a very high degree of ionization in an ECR plasma, such a system has the advantage that the ionization of the gases by the microwave power and the energy of the ions can be independently controlled. The use of direct dc bias was preferred as it has been shown to result in a narrow ion energy distribution function as compared to using rf self-bias [13]. In that study, different dc voltages were applied to two stainless steel screen grids supported above the substrate holder and also to the substrate holder. It was found that this scheme is much more effective in controlling the energy of the ions impinging on to the substrates as compared to a dc bias applied directly to the substrate holder without the screen grids [12,14].

If sources gases of CH_4 and Ar are used, instead of CH_4 and H_2 as used previously, and under strong negative dc bias at the grids, sputtering of the grids by Ar ions can be significant resulting in the incorporation of the grid metal in the growing films. The amount of metal in the films was found to be very well controlled by either varying the applied bias at the grid, adjusting the heights of the grids from the substrate holder, changing the flow ratio of CH_4/Ar or using grids with different wire spacing. The energy of the hydrocarbon ions impinging on to the substrates can also be controlled by a dc bias applied to the substrate holder.

In this work W–C:H films with different fractions of W were deposited using the above technique with two pure W grids in a gas mixture of CH_4 and Ar. The gas flow ratio was varied to control the W atomic fraction in the films, with the W fraction limited to not more than 10%. These films were characterized in terms of their conductivity, atomic concentration by Rutherford backscattering (RBS) technique, bonding configuration by X-ray photoelectron spectroscopy (XPS), and hardness. The optical gap, which is seldom reported for Me–C:H films, was also investigated.

2. Experimental procedure

Fig. 1 shows the ECR–CVD system used in the present experiment with the screen grid set-up incorporated. The details of the system can be found elsewhere [12]. Essentially, the ECR–CVD system has a downstream design whereby ions produced in the excitation chamber are extracted into the deposition chamber through the diverging magnetic field. The microwave power is introduced into the ECR magnetron excitation chamber through a quartz window. A magnetic field of 875 G required for the ECR condition is generated in the middle of the excitation chamber using the surrounding electromagnets. The divergent magnetic field configuration accelerates the plasma towards the deposition chamber where the substrates are located. Inside the deposition chamber, the substrate is placed on to a stainless steel plate which forms the base of the screen grid fixture (see Fig. 1). The grid fixture is placed on top of a circular graphite receiver with a quartz plate placed in between for electrical isolation. Four poles made of insulating Vespal are used to position the lower screen grid and upper screen grid wire mesh made of pure tungsten wires. The square W meshes have spacing between the W wires of about 10 mm. The distance between the lower grid and upper grid can be varied by adjusting the length of the supporting poles. Similarly, the distance between the sample and the lower grid can be adjusted. For this experiment, the distance between the upper and lower screen grid was fixed at 5 cm, and the distance between the lower grid and the sample holder was fixed at 1.5 cm. The lower grid was placed close to the substrate to increase the efficiency of W incorporation in the growing films. The lower and upper grids are shorted together with a negative dc voltage applied. The substrate holder was floating with no bias applied in the present experiment.

Prior to deposition, the system was evacuated to below 5×10^{-6} Torr using a turbomolecular pump. The

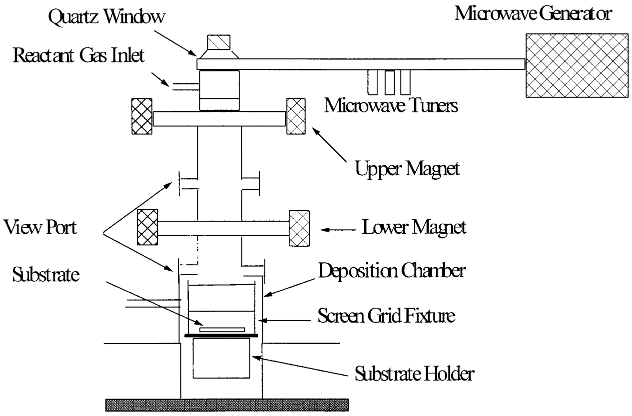

Fig. 1. Schematic diagram of the ECR–CVD system with the screen grid fixture included in the deposition chamber.

flow ratio of CH_4 to Ar was varied from 0.15 to 0.5 with the pressure maintained constant at 6 mTorr using a throttle valve. A bias of -330 V was applied to the upper and lower grids and the microwave power used was fixed at 400 W. No intentional heating was applied during the depositions, and no appreciable increase in temperature was detected at the end of the deposition process. The substrates used consist of glass and (100)-oriented single crystal silicon.

3. Results

The growth rate of the films is nominally 20Å/min and all the films were grown for about 30 min. Fig. 2 shows the atomic fraction of W for the films obtained using RBS at different flow ratios of CH_4/Ar. The atomic fraction of W decreases with increasing CH_4/Ar ratio, which is expected due to a decrease in sputtering rate of the W grids at lower Ar partial pressure. The maximum fraction of W was intentionally limited to below 10% in this study to focus on the semiconducting-like properties of Me–C:H films. With regards to changes in the chemical structure at increasing W doping level, Fig. 3 illustrates XPS results for W 4f core level spectra of the W–C:H films with W atomic fraction of (a) 0.022 and (b) 0.085. The XPS measurements were performed in a VG ESCALAB MkII spectrometer equipped with a Mg *Kα* X-ray source (1253.6 eV) and a hemispherical electron energy analyzer. The take-off angle was maintained at 75° and the constant pass energy was set to 10 eV during the spectral measurement. The binding energy was referenced to the Au $4f_{7/2}$ line at 84.0 eV. The curve fitting of the XPS peaks was performed with combined Gaussian and Lorentzian curves and Shirley background subtraction. From Fig. 3, we can see that the two components of W 4f doublet appear at B.E. $= 35.5 \pm 0.02$ eV (W $4f_{7/2}$) and 37.6 ± 0.02 eV (W $4f_{5/2}$), indicating incorporation of W into the a–C:H network. The bonding of W is found to be in form of WO_3 [15,16]. For the case of higher fraction of W in the films (Fig. 3b), the XPS spectrum shows a new component with W $4f_{7/2}$ at 33.2 ± 0.2 eV which was assigned to WO_2 [17]. The component attributed to WO_2 bonds has a weaker intensity than that from WO_3. The very small amount of W in film and broadening of W $4f_{7/2}$ peak at 33.2 ± 0.2 eV might limit the detection of WO_2 component (see Fig. 3a). The formation of tungsten oxides is attributed mainly to post-oxidation upon exposure in air. It is noted that the XPS analysis does not reveal any presence of WC bonds. The absence of WC-related bonds could be due to the low tungsten content in the films and/or the fact that no bias was applied to the substrates during the growth. Given the base pressure of 5×10^{-6} Torr, residual water contamination and metal oxidation could occur and also account for the absence of WC bonds. Our subsequent experiments on W–C:H using the same deposition system and conditions, but with bias applied at the substrates, indeed led to the formation of WC nanocrystallites, as were evident

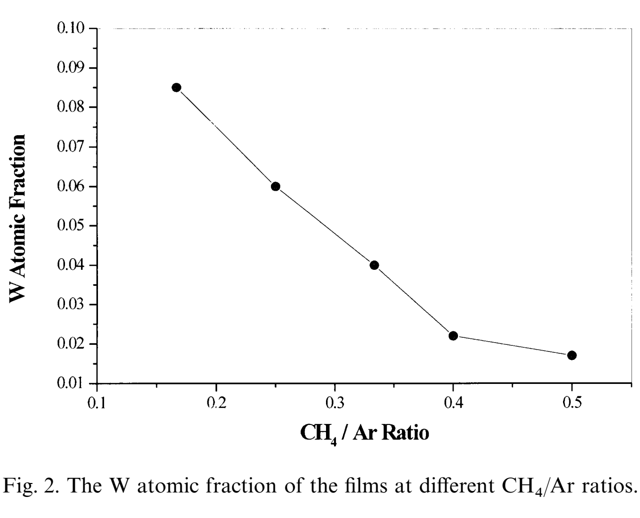

Fig. 2. The W atomic fraction of the films at different CH_4/Ar ratios.

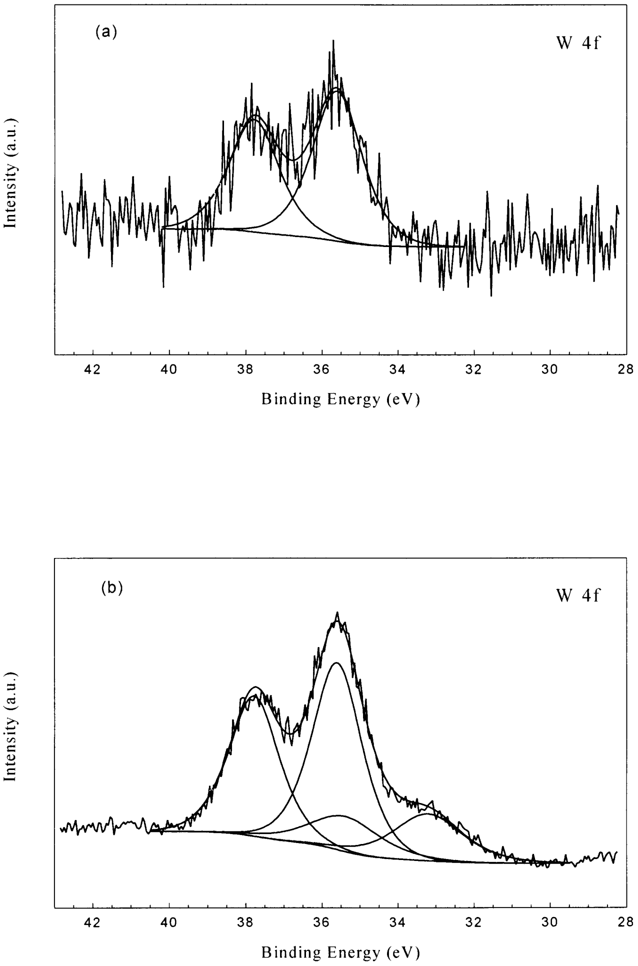

Fig. 3. XPS W 4f core level spectra of the W–C:H films with W atomic fractions of (a) 0.022 and (b) 0.085.

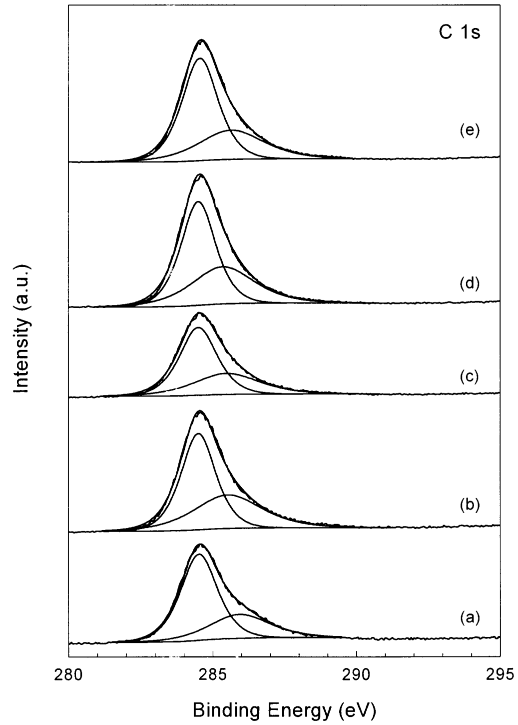

Fig. 4. XPS C 1s spectra of the films at different W atomic fractions of (a) 0.085, (b) 0.06, (c) 0.04, (d) 0.022, and (e) 0.017.

from the XRD patterns. Therefore, the results seem to suggest that certain minimum ion energy might be required to promote the growth of WC in these films.

Fig. 4 shows the C 1s spectra which were resolved into two peaks at 284.5 eV and 285.5 ± 0.3 eV. The peak at 284.5 eV is attributed to polymeric carbon whereas that at around 285.5 eV is attributed to oxidic carbon [18]. The latter is lower than the reported value of 286.5 eV [18], which could be due to the different bonding environments of the C—O bonds in the form of —W—C—O—, —C—O—W— and —C—C—O—.

Fig. 5 shows the resistivity of the films at different W atomic fraction measured using the four point probe technique. It can be seen that the resistivity decreases very sharply with increasing W atomic fraction, and a change of more than six orders of magnitude can be achieved at 8% W fraction. Indeed, even at the lowest W fraction of 2%, there is already a decrease of resistivity by about four orders of magnitude compared to the undoped films, which have resistivity typically of greater than 10^8 Ωcm. Sharp changes in the conductivity such as this have also been reported in Ru–C:H, Ta–C:H, Co–C:H and Au–C:H films at low metal fraction [1,2,10,19], and have been attributed to the modification of the a–C:H matrix through the presence of the metal in the case of Au–C:H [10]. Precolation behavior, which is marked by a sharp change in resistivity at increasing metal fraction, has been observed for Ta–C:H, Co–C:H and Au–C:H films with the transition barriers occurring at 10 vol.%, 22 vol.% and 40 vol.%, respectively [10,19]. The interpretation was supported by the observation that these transition barriers also correspond to a transition in the conduction mechanism of the films from semiconducting-like to metallic-like. As the W fraction in our films was limited to 8%, a precolation behavior is not to be expected. Preliminary studies of the conductivity change of these films over a temperature range from room temperature to 150°C reveals a thermally activated conduction process. This suggests that the films are in the regime of below the precolation threshold. The narrow range of temperature used does not allow an accurate determination of the activation energy based on the Arrhenius plot. However, a much steeper increase in the conductivity with temperature was clearly observed for films with lower W fraction. From the low W fraction measured which excludes the formation of a continuous W network, it is likely that W atoms either coalesce into isolated clusters, or atomically dispersed in the a–C:H network or possibly in a combination of both. The observed thermally activated conduction behavior could be attributed to the tunneling of electrons between the metal clusters. Although tunneling of electrons between sp^2 clusters could also account for the conduction activation behaviour, but this is unlikely in the present case due to the large conductivities observed.

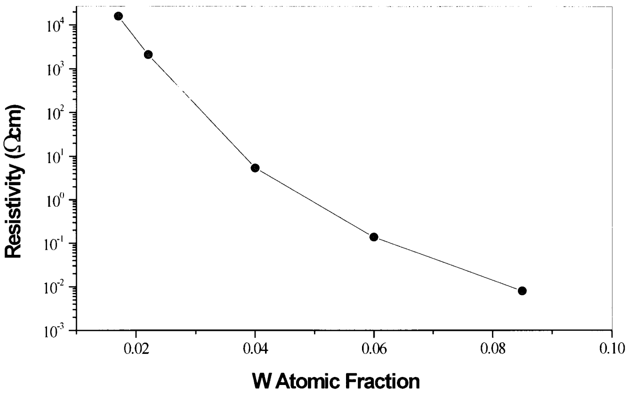

Fig. 5. The resistivity of the films measured using four point probe technique at different W atomic fractions.

The absorption coefficients of the films are calculated from their transmission and reflection spectra measured using a Perkin-Elmer Lambda 16 dual beam spectrophotometer. The absorption increases monotonically with photon energy as in the case of typical a–C:H films, and does not show any dielectric anomaly characteristics which have been observed for other systems with metallic particles embedded in a dielectric [2,20]. This could be attributed to the low W fraction in our films. The Tauc gaps (E_0) and the E_{04} gaps were determined from the absorption spectra and are shown in Fig. 6. Both the optical gaps give slightly different results, as expected, with E_{04} generally higher than E_0. More importantly, both the optical gaps exhibit a similar trend of a sharp

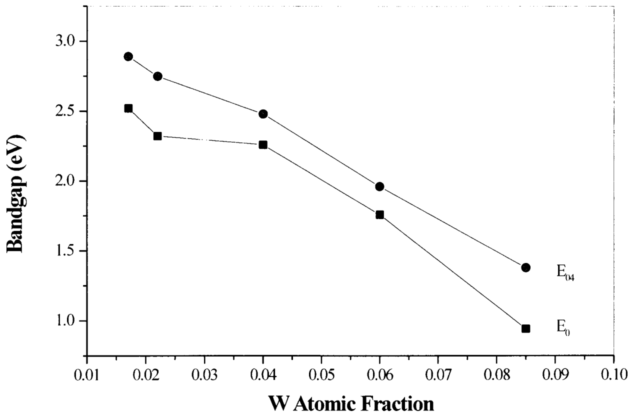

Fig. 6. The Tauc gap (E_0) and E_{04} gaps of the films at different W atomic fractions.

decrease of more than 1.5 eV at 8% W fraction, in a way very similar to that of the resistivity change. This is remarkable given the small fraction of W involved. The results suggest that similar structural changes at increasing W fraction are responsible for the observed changes in the conductivity and the optical gaps. Optical absorption results are not commonly reported for Me–C:H films and hence it is not clear how the changes in the optical gap with W fraction compares with other Me–C:H films. It is noted that there is a continuous increase in the absorption coefficient over the visible and infra-red range for Me–C:H films incorporated with increasing stainless steel fraction [21].

4. Discussion

The technique proposed in this study for the deposition of Me–C:H can be considered as a plasma reactive sputtering process. It has a major advantage of utilizing the highly ionized ECR plasma which has desirable effects on the properties of the films grown [22]. It is also flexible since the grids, instead of one of the electrodes as in other sputtering techniques, are used as the source of the metal. Therefore, this technique can be easily extended for the deposition of different Me–C:H films by using grids made of the appropriate metal. This couples with the bias at the grids allows the freedom of independently controlling the degree of the plasma ionization and the rate of sputtering of the metal. By separately biasing the substrate holder, a great variety of Me–C:H with very different microstructures can be deposited. This is not only of technological importance, but also of great interest in the fundamental study of carbide films. Deposition of films incorporated with different metals is also possible with the proposed technique by co-sputtering grids made of two different metals. One possible limitation of this technique lies in the inhomogeneity in the incorporation of the W atoms in the growing film due to the nature of the grids. However, four points probe measurements at different locations on the films give very similar resistivities, suggesting that this is not a serious problem. Another limitation comes from the poisoning of the grids, that is, the grids get coated during the process of deposition resulting in a non-uniform sputtering rate and hence affecting the incorporation of the metal in the films. This problem in principle could be overcome by biasing the grids at a very large voltage to enhance the sputtering process and hence prevent the grids from being coated substantially. By further increasing the distance of the lower grid from the substrate, the deposition of W–C:H films with very low W fraction ($<2\%$) could be possible, which is interesting in view of the large change in the properties of such films even at low metal atomic fractions. More work in this area is in progress. It should be noted that the close proximity of the W grid to the substrates, 1.5 cm in the present experiment, might not be a limitation of our deposition technique, and in principle flat parts with heights larger than 1.5 cm still could be coated. This is because in our proposed technique, the metal content incorporated is not only a function of the distance between the grids and the substrate, but it also has been shown to strongly depend on the dc bias applied to the grids and the substrate. To coat a more complex shape, the parts to be coated could be rotated to ensure a uniform and thorough coating.

The present results do not allow a definitive conclusion on the structures of these films. The thermally activated conduction behaviour favours the formation of isolated W clusters within the insulating a–C:H matrix. No detailed tribological studies have been performed for this set of W–C:H films. As the substrate was not biased in this set of experiment, hardness studies using the Nanoindenter II system showed that the films were generally not very hard, with a hardness of only about 5 Gpa, independent of the W fraction. However, subsequent depositions with a negative bias applied to the substrate holder resulted in much harder films (>10 Gpa), indicating that the ion energy remains a critical factor in determining the hardness of these films, as in the case of the deposition of pure a–C:H films. The results further suggest that the hardness of the films is still mainly determined by the microstructure of the amorphous a–C:H matrix, as least for W fraction of less than 10%. This also indicates that the direct dc bias at the substrate under the grid system is effective in controlling the ion energy, as has been demonstrated before [23], such that the hardness and the fraction of W incorporated can be separately controlled in our proposed deposition technique. It should be mentioned that the presence of oxide in these films could have some impact on their mechanical and electrical properties. These films are intrinsically sensitive to oxygen, which could react to form metal oxide either during the deposition and/or upon post-deposition. Our recent XPS depth profiling measurement on Mo–C:H films revealed a high concentration of oxygen at the surface of these films, which consequently decreased towards the bulk of the films. It is believed that similar behaviour also occurs in W–C:H films due to the high reactivity of the metal. This observation suggests that post-oxidation could be significant. The presence of oxygen could result in preferential bonding and absence of WC, and generally weaken the bonding of the structural network. This will degrade the mechanical properties of the films. On the other hand, the effect on the electrical properties could be even more significant as more oxygen atoms are located near the surface. It is believed that the conductivity of the films will decrease as a result, especially for those incorporated with a high fraction of W.

5. Conclusion

A new technique for depositing Me–C:H films based on two biased screen grids situated above the substrate holder in an ECR–CVD system has been demonstrated. It provides the advantage of a highly ionized plasma, together with the independent control of the degree of plasma ionization and the metal sputtering rate. W–C:H films deposited were shown to undergo drastic changes in their electrical and optical properties, with the resistivity and optical gap decreased by six orders of magnitude and 1.5 eV, respectively over a W atomic fraction range of 2% to 8%. These films were also found to contain substantial oxygen, incorporated during deposition or caused by post-oxidation. The presence of metal oxide not only affects the formation of WC in these films, but also could have a negative impact on their mechanical and electrical properties.

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