

Si- and W-containing carbon based nanocomposite thin films: Chemical and nanomechanical properties

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Abstract: Si- and W-containing a-C films were deposited by magnetron sputtering onto silicon wafers. The composition and chemical structure were characterized by XPS and Raman spectroscopy, while nanomechanical properties were estimated by using a depth-sensing instrument. The incorporated Si and W are preferentially bonded to carbon. Increase of Si- and W-content in the films led to well measurable increase of the hardness of the coatings.

Keywords: a-C films, diamond-like carbon, XPS, nanomechanical properties.

1. Introduction

Diamond-like carbon coatings (DLC, a-C, ta-C) owing to the combination of useful properties are gaining broadening fields of application, especially in high-tech areas. Modification of them by silicon together with different metals is in the forefront of investigations and industrial development. The aim of the latter practice is to reduce compressive stress, as well as to improve thermal stability, oxidation resistance and friction properties of the carbon coatings. Properties of the Si and N containing DLC films were demonstrated in [1,2], while the beneficial effect of Ti, W metal additives in [3,4].

2. Experimental

C-Si-W films of 200-300 nm thickness were deposited magnetron sputtering simultaneously by two magnetrons (A320 and A315, AJA International, USA) onto SiO₂ covered (111) Si substrates, using argon (of 5N purity, flow rate 25 cm³/min) as sputtering gas. The background pressure of the sputtering chamber was 10⁻⁵ Pa, while the operation pressure was 0.25-0.35 Pa. The 50.8 mm diameter high purity silicone target was driven by RF power of 20-150 W at 27.13 MHz. A diagonal strip of tungsten (of 3 mm width, approx. 2 cm²) was fixed to the target. The carbon source (diameter 38 mm) by was powered by 50-100 W DC at 500 V. The deposition was carried out at ambient temperature (25 °C). The working distance of the magnetrons were 55 and 135 mm, respectively. A negative bias in the range of 0-200 V was also applied to the substrate.

The chemical composition and the bonding states of the constituent elements were characterized by X-ray photoelectron spectroscopy and X-ray induced Auger electron spectroscopy. Spectra were recorded by Kratos XSAM 800 spectrometer using Mg K $\alpha_{1,2}$ excitation, with fixed analyzer transmission of 40 eV pass energy and

0.1 eV step size for the high-resolution spectra. The spectra were referenced to the C1s line of the adventitious carbon set to a binding energy of 284.6 eV. The accuracy of binding energy determination was ± 0.2 eV or better. Data acquisition and processing were done with the Kratos Vision 2, while quantification by the XPS MultiQuant [5] programs.

The Raman scattering spectra were recorded on a Renishaw 1000 B micro-Raman spectrometer. The 488 nm line of an argon ion laser and a diode laser with wavelength of 785 nm served as excitation sources sampling a volume of ~ 1 μ m in diameter.

Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) investigations were carried out by a Philips CM20 200 kV analytical microscope.

The nanomechanical properties, including dynamic nanohardness and reduced modulus, were measured by a NanoTest 600 (MicroMaterials Ltd., UK) tester. For depth-sensing nanohardness tests a Berkovich type indenter head was used. Indentations were made with maximum load of 3 Nm and 0.033 mN·s⁻¹ loading /unloading rate. Oliver-Pharr fit [6] was applied for data evaluation with the accuracy of ± 5 %. Scratch and wear tests were performed with Rockwell conical diamond tip using maximum load of 20 mN.

3. Results and Discussion

XPS studies

The silicon content of the C-Si films varied between 20-40 atomic %, depending on the applied source power. The tungsten content in the C-Si-W films varied between 2-50 atomic % while the silicon content at the same time between 25-0 atomic %.

The broaden asymmetric spectral lines of the ‘as deposited’ samples (Fig. 1) were decomposed to

components representing individual chemical states. The high BE shoulder of the Si2p at 102 eV corresponds to Si–O bonds, developed on the oxidized surface. The spectrum of W4f doublet also has high energy components, representing a small amount of oxidized state. Part of the surface carbon is also oxidized, illustrated by two high BE components at about 285 and 287 eV, what may be assigned to C–O and O–C–O type moieties, respectively. The two components of the O1s line corresponds to the O–C and O–Si, together with the O–W bonds.

Majority of the oxidized surface layer could be removed by a moderate Ar⁺ ion etch (2.5 keV, 5 min). This state is representative for the films developed at deposition. The corresponding spectra are shown in Fig. 2. The oxygen content of the films was insignificant, typically below 3 atomic %.

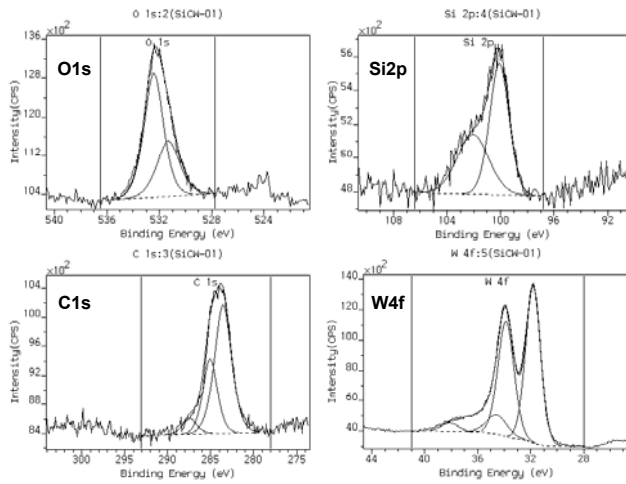


Fig. 1 XP spectra of the 'as deposited' sample with 20 at% Si and 16 at% W content

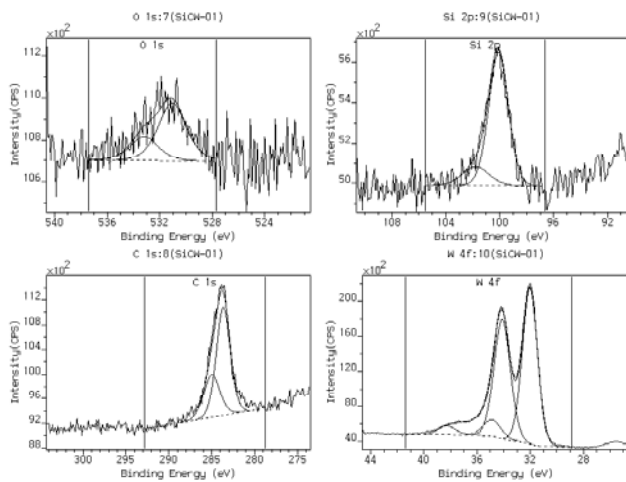


Fig. 2 XP spectra after short ion etch. Composition changed to 10 at% Si and 41 at% W

Predominant C–Si (Si2p 100.8 ± 0.2 eV) and C–W (W4f 32.3 ± 0.2 eV) chemical bonds could be identified by the chemical shifts of the XP spectra. This is consistent with the Si Auger parameter, derived as a sum of Si2p photoelectron and SiKLL Auger line energies, varying between 1714.8–1715.8 eV, indicating carbide formation in the system, see Fig. 3.

The chemical shift of the C1s line (284.2 ± 0.2 eV) can be assigned either to Si–C or sp² C–C bonds.

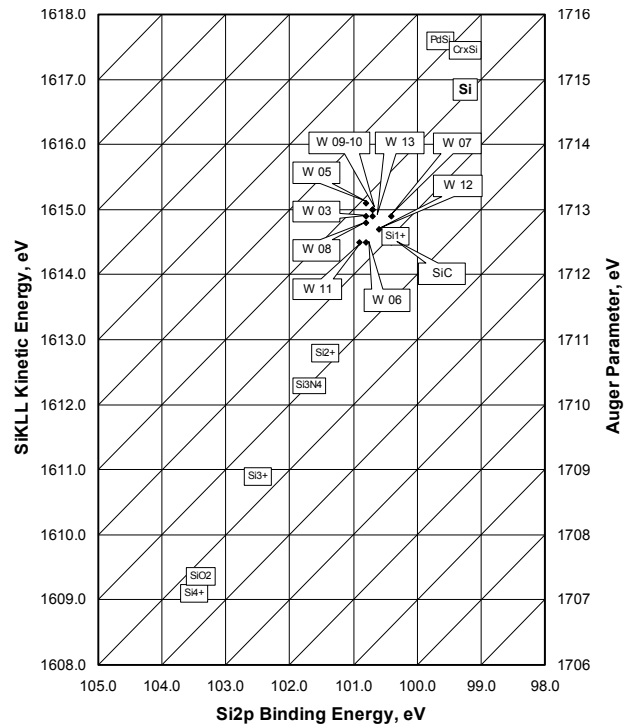


Fig. 3 Si2p - SiKLL Auger parameter plot of various C–Si–W films together with literature data

Raman studies

As far as the crystalline W₂C does not show Raman activity the spectra basically represent the bonding states of the carbon containing matrix. Spectra of the samples containing only Si are basically similar to the ones of diamond-like carbon (DLC) coatings with somewhat prevailing intensity of the D band at around 1400 cm⁻¹, and the G component, centered at about 1520 cm⁻¹ overlaps with the D band. Addition of W modifies significantly the spectra, shifting G component to higher wave numbers [7,8].

Transmission electron microscopy

The transmission electron microscopy and selected area electron diffraction investigations proved that the films with intermediate (24 at %) and high (41 at %) W content are amorphous nanoclusters. At lower W content the clusters are elongated of 1–5 nm size (Fig. 4).

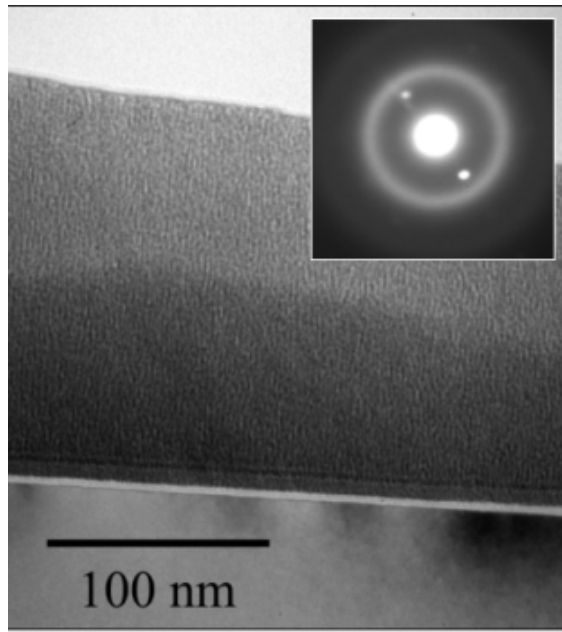


Fig. 4 Cross section micrograph and SAED pattern of sample with 23 at% Si and 24 at% W content deposited at -50 V bias.

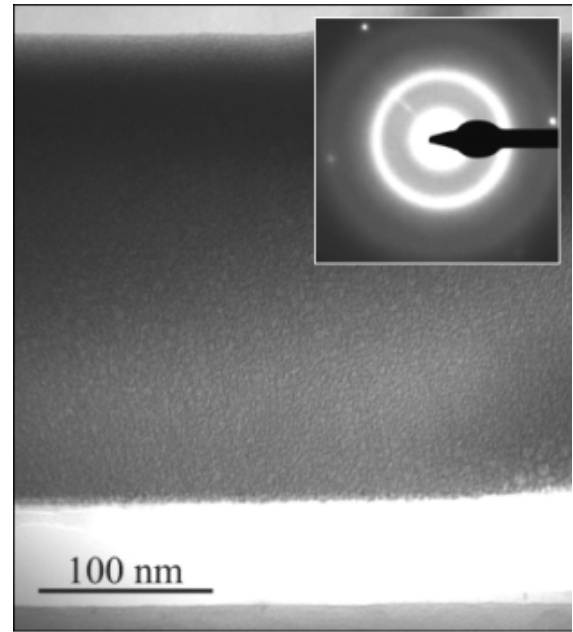


Fig. 5 Cross section micrograph and SAED pattern of sample with 10 at% Si and 41 at% W content deposited at floating potential

Films deposited on floating potential does not show this clustering and elongated nanostructure (Fig. 5).

Nanomechanical studies

The nanohardness (H) and reduced modulus (E) of the films were significantly higher than that of the silicon substrate being 10 GPa, 127 GPa, respectively. H and E values were for a-C film 16 GPa and 155 GPa, for (Si)-(a-C) films 13-16 GPa and 140-185 GPa, and for (Si+W)-(a-C) films 12-19 GPa and 160-210 GPa, respectively, depending on the chemical composition.

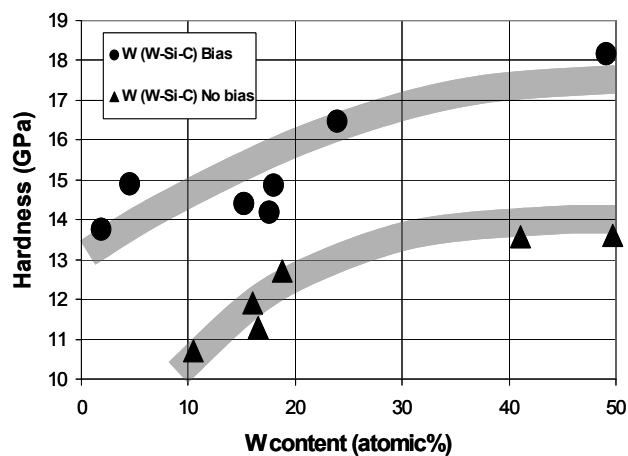


Fig. 6 Change of nanohardness of the layers vs. the W content of the samples

Significant differences were observed between the C-Si and C-Si-W films: while the applied substrate bias did not affect the hardness of the C-Si films, considerable increase of the hardness was measured for C-Si-W coatings when biasing the substrate, as depicted in Fig. 6.

The hardness of the C-Si films were close or equal to that of the C-Si-W films deposited with bias.

W containing films, although usually softer, show higher scratch resistance: while C-Si films delaminate at about 15 mN load (Fig. 7), no delamination was observed for C-Si-W films up to 20 mN (Fig. 8).

4. Conclusions

- (Si)- and (Si+W)-containing series of a-C films were deposited on oxidized Si substrates at ambient temperature by dual magnetron sputtering with Si-content up to 42 at% for the (Si)-(a-C) series, and up to 25 at% Si and up to 49 at% W for the (Si+W)-(a-C) series by varying the input power of the magnetrons.
- In accordance with simplified thermodynamic considerations, the incorporated Si and W are preferentially bonded to carbon in our a-C films, as manifested by the XPS chemical shifts. Formation of phase-separated clusters of silicon, silicon carbide, tungsten, tungsten carbide or tungsten silicide, however, could not be detected.
- Incorporation of Si and, especially W, lowers the graphitic carbon content as shown by the decreasing intensity of the G component in Raman spectra.

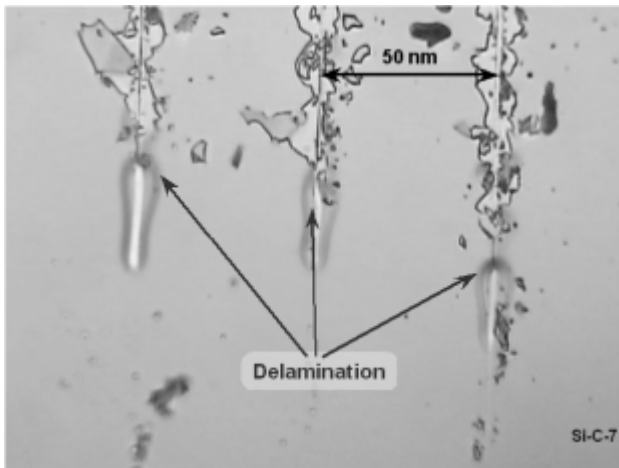


Fig. 7 Scratch tracks on C-Si film, 15 at% Si

- Well aligned, 1–5 nanometer size, fibrous morphology was developed in W-containing films, as revealed by TEM. The coatings proved to be completely amorphous by electron diffraction.
- Increase of the Si- and W-content in the films led to well measurable increase of the hardness of the coatings. Application of -50 V to -100 V bias to the substrates at deposition resulted in a pronounced increase of the hardness for W containing films having comparable compositions.
- While delamination of the a-C and (Si)–(a-C) coatings were observed in scratch tests at loads well below 20 mN, no delamination was observed for W-containing films even after the fifth loading cycle in the wear tests.

Acknowledgement

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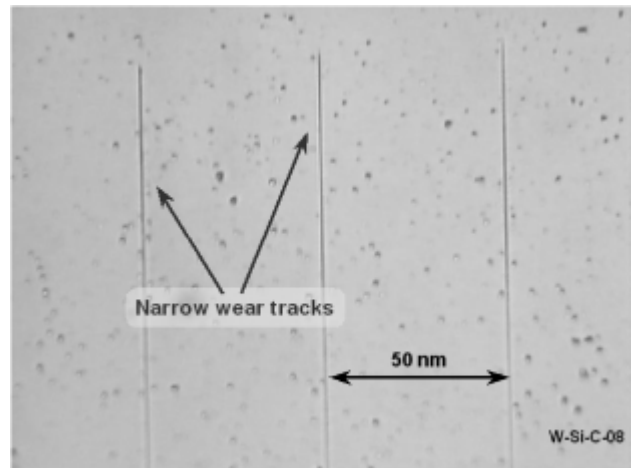


Fig. 8 Scratch tracks on C-Si-W film, 22 at% Si, 16 at% W

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