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THERMAL OXIDATION OF TUNGSTEN COATINGS FOR DETECTION BY INFRARED SPECTROMETRY METHOD

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Abstract. Physical vapor deposition (PVD) of metallic thin films is used extensively in the fabrication of semiconductor technology devices - use as of lately for them have grown. Tungsten (W) is a low resistivity, refractory metal, that is often deposited by PVD methods for use as a gate contact to semiconductor devices and due to the low work function and high thermal stability, W can be used for the fabrication of field emitters in microelectronics [1–3]. In order to monitor quality of the synthesized thin films by magnetron sputtering method, it is necessary to develop methodology suitable for the analysis of these thin films. Infrared spectrometry is a sensitive method for the analysis of chemical bonds, but W thin films contain weakly polar and non-polar W-W bonds, that cannot be directly detected by infrared spectrometry, therefore oxidation of W is selected as thermal oxidation method for detecting oxidized products for thin films of thickness 150 nm, for instance, W-O bonds. After oxidation, it was observed, that the oxidation of W thin films takes place already at a 600 °C in the air atmosphere. The Fourier transform infrared spectrometry (FTIR) spectra of modified coatings showed formation of additional new signals in the region of 700-900 cm^{-1} attributed to W-O, O-W-O, W=O bonds - formation of W-oxygen bonds on Si-SiO_2 substrate was achieved. For coating homogeneity and production quality formation, additionally synthesized control samples are recommended for FTIR analysis.

1. Introduction

As of lately, interest in audio devices has increased. Tungsten (W) thin films are used in microelectronic devices as electrical compounds, interconnections and diffusion barriers [4]. The wide application is possible, because W thin films have several excellent properties, such as high thermal stability, low thin film voltage [3, 5]. W superconducting thin films are widely studied in fundamental science, is a current topic in scientific projects, they are used in high-energy plasma research, and are intended to be used also in International Thermonuclear Experimental Reactor (ITER) [6].

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More importantly, W is expected for use in the manufacture of triodes - their structures, the dimensions of which may vary on the nanometer scale. Characterization of the crystal structure of W is important to improve the knowledge about stability properties of layers, the quality depending on production process and their composition. Sensitivity against changes in surface structure is essential in the development of stable operating devices using W. On nanometer scale precipitated W on dielectric silicon (Si) - silicon dioxide (SiO_2) layer bases enable high thermal resistance and other conditions for fabricating semiconductor integrated audio amplifiers and microtriodes [7]. In the process of production, it is essential to check the homogeneity and quality of the synthesized films for further production of microtriodes from W thin films on Si-SiO_2 substrate.

W has non-polar bonds (W-W), oxidation as thermal modification method can be applied for detection of W thin film oxidized products on Si-SiO_2 substrate for Fourier transform infrared spectrometry (FTIR), such as polar bonds of W-oxides. Importance of delineation of the spectra of W thin films on Si-SiO_2 is required in order to better characterize the changes in W thin films and their oxidation products on the substrate after thermal modification.

W exists in both α-W and β-W phases [8]. The formation of the β-W phase is affected both the surface of the substrate and the presence of trace impurities. β-W phase transforms into α-W phase up to 630 °C [9]. For magnetron sputtering, W thin films can be deposited as α-W, as β-W or as a mixture of the two phases, depending on the pressure, applied voltage or impurity atoms presence in the synthesis chamber, layer thickness, temperature [10–12]. The properties and phase composition of W thin films strongly depend on type of preparation, as well as the used substrate [13]. Heating W in air to 300 ℃ results in amorphous WO_3. In W coatings, oxidation occurs between 700 ºC and 1000 ºC, usually forming two oxide layers. In the outer layer, porous powdery W oxide (WO_3) in yellow colour is formed, while a thin oxide layer without a specific stoichiometric composition forms in the inner layer [14].

W thin films can be divided in α-W and metastable β-W phases [15]. Due to microstructure inconsistency, β-W tends to have completely different electrical and mechanical properties compared to α-W, for example, α-W has higher electrical conductivity [16], but metastable β-W has higher hardness (24.5±1.6 GPa) compared to α-W configuration (21.3±1.1 GPa) [17]. Large grain size (150-250 nm) characterizes α-W thin films, sizes below 10 nm (5-10 nm) - the β-W phase. β-W phase usually exists on the Si substrate, but when a thicker W thin layer is sputtered on the SiO_2 base, the α-W phase is stably observed [4, 8, 13].

Magnetron sputtering as physical vapor deposition (PVD) method is widely used to form W metallic films, because of W high melting point. Physical thin film properties of their layers are complicated, in practice, it is impossible to keep all the factors identical for sputtered W coatings according to the different methodologies described publications, however, producing them in the same factory with analogous production conditions is possible to achieve repeatability. Therefore, it is difficult to obtain a thin film of W with the expected features, citing early research. As in generally known, the properties of the sputtered W thin films are closely related to the surface morphology and strain of the surface [4].

In this research, W thin films on Si-SiO_2 substrate deposited by PVD were oxidized using various conditions for detection of W thin film W-oxygen bonds, their possible analysis with FTIR method and W thin film thermal characterization for creating further innovative microtriodes on this material.

2. Experimental

2.1. Materials – W thin films

W thin film coatings synthesized on Si-SiO_2 substrate by magnetron sputtering method were analyzed. The substrate (Si-SiO_2) was obtained thermally growing a 0.75 µm thick SiO_2 layer on Si wafer (washed in CARO solution before SiO_2 dielectric layer deposition) with (111) crystallographic structure, round bases surfaces (diameter is 76 mm) at a temperature of 1130 °C in humid oxygen environment, exposure time – 2h. Sputtering time is 45 s and thin film (W) coverage layer thickness - 150 nm. Samples Si-SiO_2-W (figure 1-a) are used for testing the methodology and evaluating the analysis of the applied methods.

The samples Si-SiO_2-W-e (figure 1-b) needed in the further production process are synthesized analogues with the previous thin films by the magnetron sputtering method (its duration is 45 s and coating layer thickness - 150 nm), where W in specific areas of the sample surface are chemically treated - etched (e) off. In the subsequent analysis process, emphasis placed on the particular W thin film band analysis.

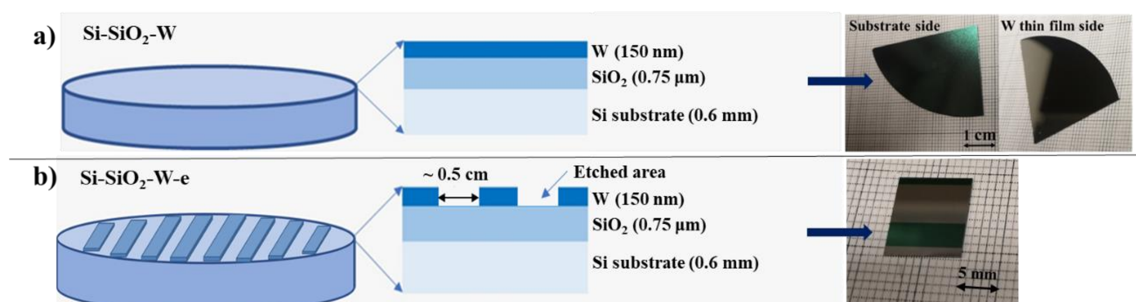

Figure 1. Schematic illustrations and photos of W thin film samples: a) Si-SiO_2-W, b) Si-SiO_2-W-e

Synthesis process of the samples was carried out by Joint-stock company "ALFA RPAR".

The samples are divided according to their application for a specific analysis (figure 2), evaluating the previously obtained results during the research [18].

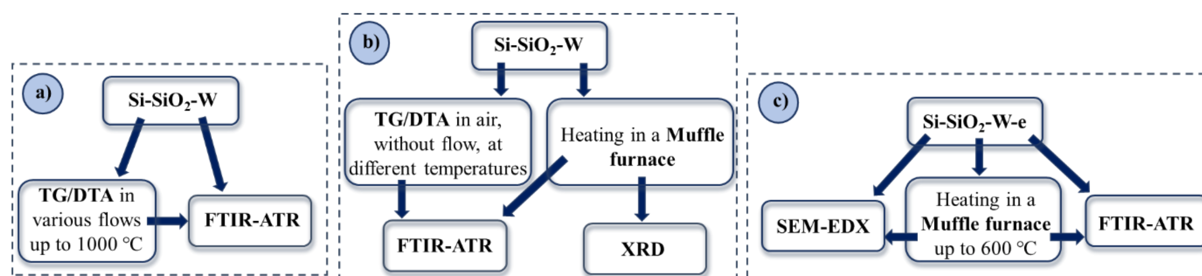

Figure 2. W thin film method analysis schemes

Measurements were made for the sample: both for the surface covered with a thin film (W) and the substrate (Si-SiO_2) to assess signal correspondence to each. Synthesized thickness of the layers is guaranteed by the manufacturer "ALFA RPAR", previously measured by the profilometry method and additionally not checked within the research. Samples are analyzed for chemical bonds at elevated temperatures and the crystal structure of the samples. Plates of samples are split for selected analyses in suitable sizes for the methods: for Thermogravimetry/differential thermal analysis (TG/DTA) around 4x4 mm, for heating in a Muffle furnace and for X-ray diffractometry (XRD) analyzes around 20x20 mm, for the FTIR method, fragments of different sizes are used depending on the previously applied methods (figure 2). Glass cutting scalpel is used for cutting samples.

2.2. Methods

FTIR spectra were obtained using a *Bruker VERTEX 70v* spectrometer equipped with an attenuated total reflection (ATR) module consisting of diamond crystal with a refractive index of 2.4. The spectrum is recorded in a range of 4000-400 cm^{-1}, with a resolution of ±2 cm^{-1}, in a vacuum of 2.95 hPa, 20 easurements per spectrum. Measurements were performed for coatings, each at 3 points on the sample.

For TG/DTA the sample fragments were placed in Al_2O_3 ceramic crucibles according to their size, diameter 5 mm. Heating of *SEIKO EXSTAR TG/DTA 6300* was 10 °C·min^{-1}, up to a specific

temperature. Heating of Si-SiO_2-W samples was carried out until 1000 °C in different flows (figure 2-a), which has been summarized previously[18] and, inferring from the obtained results, the samples further heated up to 200, 400, 600, 800 and 1000 °C in stationary air conditions (figure 2-b). After reaching the temperature and cooling the samples, recording of FTIR-ATR spectra were done.

Plate fragments were also heated in *Nabertherm GmbH SN388625* Muffle furnace. It was used to heat samples larger than in TG/DTA analysis (~20x20 mm in size) so that it can be placed and analyzed in the cuvette intended for XRD, as well as in scanning electron microscopy (SEM) combined with energy dispersion X-ray spectrometry (EDX); the data were analyzed and compared. Si-SiO_2-W samples were heated at 10°C·min^{-1}, at different temperatures, with a holding time of 1 h in laboratory air without flow, analyzed by XRD, as well as repeatedly obtained FTIR-ATR spectra (figure 2-b), but Si-SiO_2-W-e samples heated up to 600 °C at 10 °C·min^{-1}, with holding times 1, 3 and 6 hours - after taking FTIR-ATR spectra and SEM-EDX images (figure 2-c).

Obtained X-ray diffractograms of crystalline were measured at ambient temperature on *Bruker D8 Advance* using Cu Kα radiation (1.54180 Å), equipped with a LynxEye position-sensitive detector. The tube voltage and current were set to 40 kV and 40 mA. The divergence slit was set at 0.6 mm, and the antiscatter slit was set at 8.0 mm. The diffraction patterns were recorded using a 0.2 s/0.02° scanning speed from 10° to 60° on 2θ scale.

Morphology and elemental distribution of samples were evaluated by a high-resolution field emission SEM apparatus *Thermo Scientific™ Helios™ 5 UX,* at 2 kV electron acceleration voltage, 25 pA current by detecting secondary electrons using through-the-lens detector (TLD), an ion conversion and electron (ICE) detector, while the energy-dispersive X-ray spectroscopy (EDS) was performed at an acceleration voltage of 15 kV. Measurements were made for Si-SiO_2-W-e sample before and after heat treatment at several points on the sample surface. EDX mapping was done at several sample points.

3. Results

Thermal oxidation methods were applied for both types of W thin films. A comparison between synthesized 150 nm W thin films were done, comparing chemical bonds and surface morphology.

3.1. Thermal oxidation of Si-SiO2-W samples in various flows

For the samples analyzed in different environments, it is expected, that the oxygen in the same samples from the substrate SiO_2 together with the thermal oxygen added during processing will oxidize W thin films to form oxides detectable for FTIR-ATR in air oxidation without flow. Comparing the initially captured Si-SiO_2-W spectra before thermal oxidation with already modified ones previously, there were observed changes compared to the original spectrum. W-oxide bonds were detected and oxidation in laboratory stationary air conditions (no flow) was considered sufficient [18].

3.2. Thermal oxidation of Si-SiO_2-W samples in different temperatures

After thermal oxidation over 600 °C W-O bonds attributable to WO_3 oxide were detected in FTIR-ATR spectra, but at higher temperatures, W=O bonds as well as W-O bond formation occur [18], which could correspond to another W-oxide (figure 3-a). Si-O shown in the spectra indicate the detectability of the substrate or its possible additional oxidation, or thin film separation from substrate at higher temperatures.

No new bonds occured after Muffle furnace heating compared to TG/DTA, as an example shown of 800 °C spectra (figure 3-b), but there were small differences in intensities noticeable, which can be explained by the sample sizes, where in TG/DTA, they were smaller, and, starting at 600 °C, there is a faster detection of new bonds - it can be concluded that regardless of the heating environment, FTIR-ATR detectable W-oxide bonds will form.

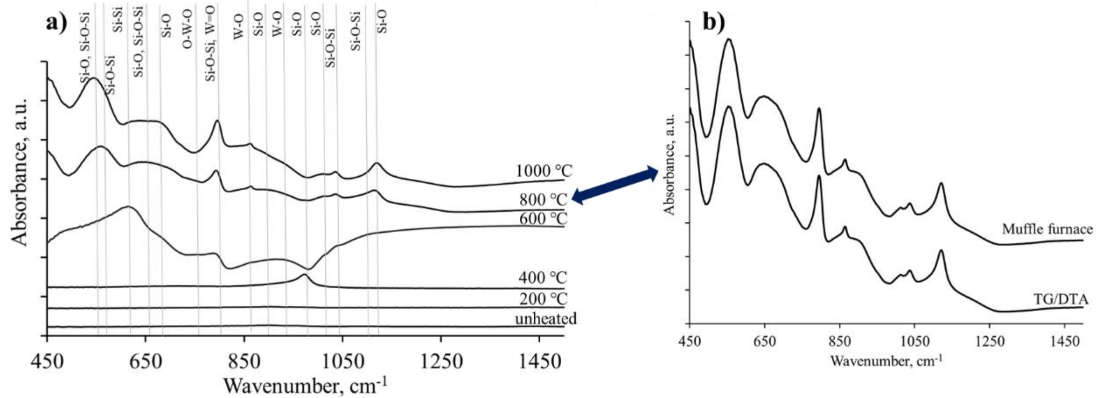

Figure 3. FTIR-ATR spectra of: a) $Si\text{-}SiO_2\text{-}W$ sample after thermal oxidation in TG/DTA at different temperatures with bond transcripts, b) FTIR-ATR spectra of $Si\text{-}SiO_2\text{-}W$ thin film coating after thermal analysis in Muffle furnace and TG/DTA equipment, heating up to 800 °C

In X-ray diffractograms of samples heated at 200, 400, 600 °C as well as of the unheated sample (figure 4), reflex characteristic to a Si (111) at 28º 2θ. Other Si reflexes were not captured due to the dominant orientation present in Si film. Unheated sample also shows reflexes corresponding to both α-W and β-W. However, when heated at 200 and 400 °C, sample shows only a pronounced α-W characteristic (110) reflex at 40º 2θ. After heating to 600 °C, Si or SiO_2 characteristic reflexes, as well as previously detected W reflexes were no longer manifesting. Instead, reflexes of both orthorhombic and cubic WO_3 reflexes were present. From here, it can be concluded, that oxidation of the W-coated thin films to WO_3 occurred at temperature higher than 400 °C and lower than or equal to 600 °C, identified phases correspond to the information found in previous researches [19].

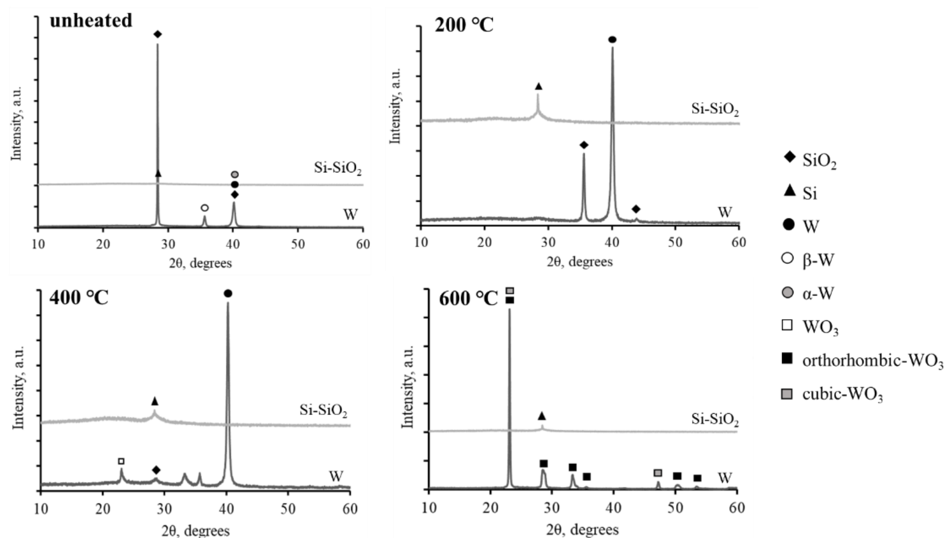

Figure 4. X-ray diffractograms of the W thin films and substrate of the $Si\text{-}SiO_2\text{-}W$ sample with transcripts

X-ray diffractograms were not captured for higher temperatures in the heating series, because the presence of W oxide was determined in all $Si\text{-}SiO_2\text{-}W$ samples heated at 600 °C.

The phases determined by the X-ray diffractograms complement results obtained by the FTIR-ATR method: a WO_3 crystalline phase is formed, as well as reflexes of the substrate are detected. 600 °C temperature is sufficient for oxidizing the samples.

3.3. Thermal oxidation of Si-SiO2-W-e samples at 600 °C temperature

Previously used methods successfully allowed to thermally modify and analyze the thin films, when performing the specific series of analysis, but in order to more accurately detect the changes that occurred on coating surfaces, for specific new samples, in parallel with the FTIR-ATR analysis method, SEM-EDX method was used.

After treatment in Muffle furnace at temperature of 600 °C at different time intervals of 1, 3, 6 hours on the surface of the Si-SiO_2 substrate, from which previously was etched W thin film, no significant changes occured. Comparing heated samples to unmodified Si-SiO_2-W-e, intensity of the FTIR-ATR spectra was noticeable in the 1166 cm^{-1} Si-O-Si bond shoulder, which is also characteristic of the data, with a peak at 1172 cm^{-1} [20] both on the substrate surface and for a thin film.

Pronounced changes can be observed in the FTIR-ATR spectra of the W thin film after heating, where W-O, W=O and O-W-O bonds are observed, as well as new Si-O and Si-O-Si bonds[18] (figure 5) compared to the obtained FTIR-ATR spectrum of the substrate before (unheated sample) oxidation.

For Si-SiO_2-W-e samples in places, where the thin layer of W has been etched off, do not observe

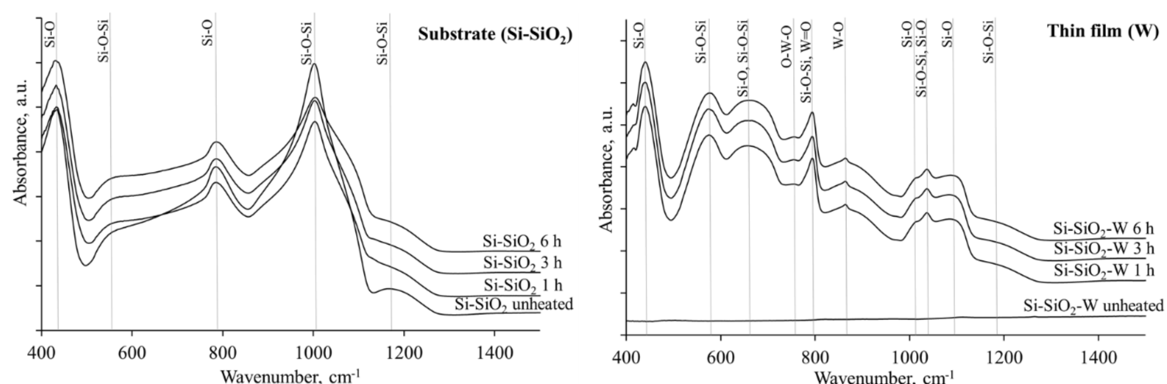

Figure 5. FTIR-ATR spectra of Si-SiO_2-W-e analyzed samples with their transcripts

significant changes attributable to the presence of W or its new oxide bond formation, which indicates, that the thin film has been successfully etched in the specific areas and the methodology used can still be applied in industry.

For analyzed W thin film surfaces in Muffle furnace depending on the duration of heating, observed significant differences in the FTIR-ATR spectra were not, and regardless of the heating environment and duration, FTIR-ATR detectable W oxides will form when heated to 600 °C. However it is essential to consider, that after heating W for a thin film, regardless of the temperature and of heating duration, new bonds attributable to the substrate can be observed, thus in the following studies related to FTIR, it would be important to compare similarly synthesized samples with different ones, checking how big the effect is on the detectability of W thin films on specific substrate.

There were differences Si-SiO_2-W-e in SEM images on the etched interfaces after thermal modification (figure 6). Slight oxidation and delamination of W thin films can be observed on the interface between W thin film and Si-SiO_2 substrate, which may indicate the formation of W-oxide or additional oxidation of SiO_2 in air.

The atomic mass (%) gives the result, that W/oxygen molar ratio is 1:3.3 ($WO_{3.3}$), from which it can be concluded that $WO_{2.9}$ was formed (slight blue-violet colour) before changing to WO_3 (yellow colour) as thin film colours are observed changes compared to the original sample. The W-oxygen bonds seen by FTIR-ATR correspond to the resulting oxide, and also has an additional oxygen signal, possibly detected from SiO_2 of the substrate (figure 7). Therefore, it is verified that the bonds detected in the FTIR-ATR method correspond to compounds formed by Si, W and oxygen. However, it should also be

concluded that EDX is a volume analysis and there could be a lot in the volume under consideration interfering oxygen atom, for example from the already mentioned Si-SiO_2 substrate.

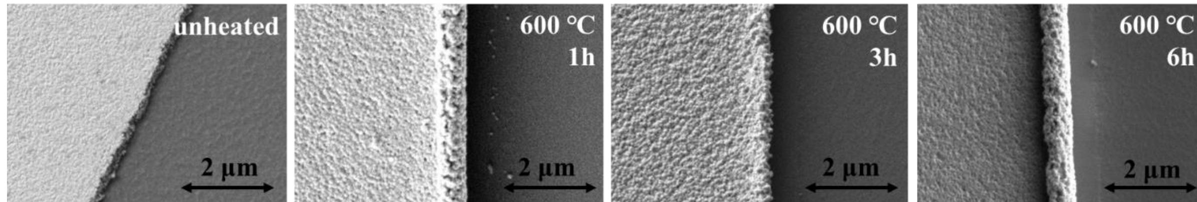

Figure 6. SEM of Si-SiO_2-W-e samples - W thin film and interface with Si-SiO_2 substrate

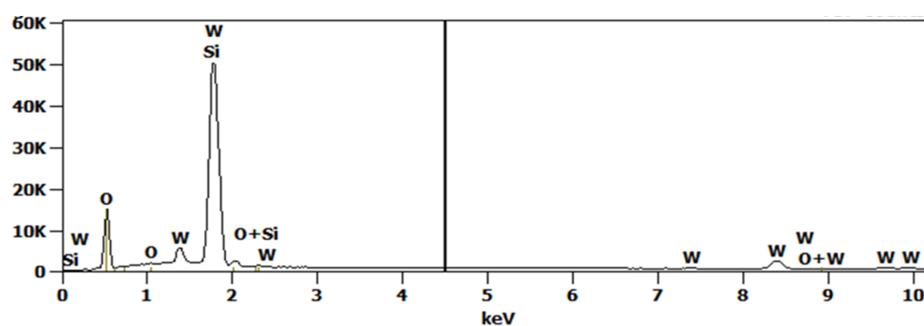

Figure 7. EDX spectrum of Si-SiO_2-W-e sample - W thin film, after heating at 600°C for 1 h

Thermal oxidation methods are sufficient for analysing W thin films. For qualitative determination of W-oxide formed bonds, FTIR-ATR method can be applied. SEM-EDX data give information of interface of thin film and substrate possible oxidation and delamination, giving information about thermal stability of the films in elevated temperatures.

4. Conclusions

For the characterization and quality control of the synthesized W coatings on the Si-SiO_2 substrate by FTIR method and further fabrication of microtriodes, it is necessary to modify the coatings to achieve polar, FTIR-ATR detectable bonds, as well as characterize the thermal properties of W thin films. Oxidation of W thin films in air occur at temperature up to 600 °C during heat treatment of films in stationary conditions. Chemical changes were observed in the FTIR-ATR spectra of the modified films in the area 700-900 cm^{-1}, W-O, O-W-O, W=O bonds formed as a result of oxidation, the formation of which corresponds by XRD and EDX results.

Acknowledgments
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