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FTIR Analysis of Oxidized Tungsten and Tungsten Diboride Nanolayers

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Tungsten (W) and tungsten diboride (WB_2) materials can be used to fabricate electron emission layers in field emission microelectronic devices. The characterization and quality assurance of synthesized films is crucial for the good performance of the devices. W and WB_2 nanofilms with a thickness of 150 nm and 200 nm were deposited on the Si-SiO_2 substrate by the magnetron sputtering technique. The synthesized layers were thermally treated in a thermal analysis device under various gas flow conditions (varying Ar; N_2; synthetic air; air with O_2, N_2, and moisture (further in this text – laboratory air)) and after oxidation, FTIR (Fourier transform infrared spectrometry) spectra were registered. FTIR spectra of the as-deposited layers showed weak peaks related to Si-O and Si-O-Si bonds from the substrate and considered for the analysis of the layers. Several new peaks occur in the spectra of the thermally treated layers. Of the oxidation layers, new peaks related to nanolayers, were observed W-O bonds, it is noticeable that the spectra vary with each other with signal intensity and offsets. In each experimental environment with various gas flow conditions, there were W=O bonds observed, also in every environment except in laboratory air with the flow, B-O bond was detected for about 1300 – 1350 cm^{-1} range. It was shown that thermal oxidation of W and WB_2 layers can be applied for the analysis of W and WB_2 layers on SiO_2 substrate by forming W and B oxides using treatment in high temperature and detection of their bonds by FTIR.
Keywords: tungsten, tungsten diboride, infrared spectrometry, thermal treatment, nanolayers.

1. INTRODUCTION

Advances in micro and nanotechnology are inspiring a renaissance in vacuum electronics. Field emission devices are used in micro and nanoscale vacuum electronic circuits [1, 2], such as low noise amplifiers with low sensitivity to external noise, which is important for operation in harsh environments such as elevated temperatures or space applications. Tungsten (W) and tungsten diboride (WB_2) can be used for the fabrication of field emission layers due to the low work function and high thermal stability of these materials [3]. W and WB_2 can be deposited on dielectrics, such as Si-SiO_2, that is used also for the fabrication of nanocapacitors [4].

FTIR (Fourier transform infrared spectrometry) is a modern method that has been widely used in recent years with the development of computer technology. It is used to characterize chemical bonds in nanolayers. The technique is also used for the analysis of organic and polar compounds. Additionally, by applying a modification of chemical bonds in the analyzed sample, FTIR can be used for the analysis of non-polar compounds as well and it has been already applied for analysis on nanolayers [4]. Since W and WB_2 have weakly polar (W-B) or non-polar bonds (W-W), modification (oxidation) of the bonds can be performed such as thermal analysis for achieving the oxidation process of various materials at high temperatures. It is possible to achieve the formation of polar bonds such as W-O, B-O at elevated temperatures by varying the content of oxygen and water, and then the FTIR spectra of the oxidation products can be measured and detected [5]. The spectra of oxidation products can be used for characterization of the initial W and WB_2 nanolayers by detecting certain oxides, the presence of certain elements in the samples can be proven. Also, the intensity ratios of the FTIR signals of the synthesized oxides could be used to determine the presence of certain elements in the synthesized films (quality control of the synthesis process), as well as element stoichiometry in the initial films. However, the challenge is to determine oxide-on-oxide, therefore a detailed examination of the modification of W and WB_2 layers on SiO_2 is necessary.

In this research, the initial W and WB_2 nanolayers, fabricated with the thickness of around 150 nm are thermally treated under various conditions and analyzed with FTIR method. From the obtained results recommendations for the optimal procedure for analysis of metal-containing nanofilms on SiO_2 can be developed.

2. EXPERIMENTAL DETAILS

In total, 6 types of samples were studied: 2 coated with W nanolayers and 4 coated with WB_2 nanolayers; sample parameters are given in Table 1.

W and WB_2 layers with a thickness of around 150 nm were deposited at Joint-stock company "ALFA RPAR, the thickness of layers measured with a profilometer.

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Additionally, to the 150 nm films a 200 nm film was analyzed to compare, if a thickness related effect can be observed.

Table 1. Sample parameters, magnetron sputtering method on Si-SiO_2 (d = 0.75 μm)

Sample type identificator	Nanolayer	Sputtering time, s	Layer thickness, nm
1_W 2_W	W	45	150
3_WB_2 4_WB_2 6_WB_2	WB_2	45	150
5_WB_2	WB_2	60	200

Layers were fabricated on the Si (76 mm) wafer (111 wafer surface). Synthesis was performed on the Si-SiO_2 substrate by the magnetron sputtering technique. Si-SiO_2 substrate was obtained by thermally growing a 0.75 μm thick SiO_2 layer on the surface of a Si wafer at 1130 °C. Wafers were cut into pieces of ~3 × 3 mm and thermally treated in varying conditions and analyzed with infrared spectrometry. Thermal treatment performed in a thermogravimetry and differential thermal analysis (TG/DTA) device SEIKO EXSTAR 6300 under 4 various gas flow conditions (varying the content of O_2 and moisture) as well as it was possible to apply stationary conditions – laboratory air without flow. Experimental details are given in Table 2.

Table 2. Environment parameters for the thermal treatment

Flow, mL/min	Gas	Description	Relative humidity, %
100	Nitrogen	N_2, 99.99%	< 5 %
100	Synthetic air	20.9% O_2, 79% N_2	< 5 %
100	Laboratory air	Main components: N_2, O_2, H_2O, CO_2	~ 45 %
100	Argon	Ar 99.,99%	< 5 %
0	Laboratory air	Main components: N_2, O_2, H_2O, CO_2	~ 45 %

The device is with a horizontal beam balance setup. Sample with mass of around 3 mg placed in Al_2O_3 crucible (diameter 5 mm). Heating rate 10 °C/min, up to 1000 C. For each of the environments a measurement with an empty crucible (background measurement) was performed. Prior to and after oxidation, FTIR spectra were acquired with Bruker Vertex 70v equipped with an attenuated total reflection (ATR) module with diamond crystal, wavenumber range 4000 – 400 cm^{-1}, resolution ± 2 cm^{-1}, in a vacuum of 2.95 hPa, 20 measurements per spectrum. A background spectrum was measured prior to the sample measurements and subtracted by Opus (Bruker) program. At least 3 spectra per sample were measured. Average spectrum calculated and used for further analysis. The deviation of the absorbance value is estimated to be around 20 %.

3. RESULTS AND DISCUSSION

During the thermal treatment mass changes, mass change rate as well as the thermal signal difference between crucible with sample and reference, empty, the crucible was recorded. However, the recorded changes were negligible, compared with background measurements, therefore the main analysis focused on the analysis of FTIR spectra measured prior to and after thermal treatment.

In the spectra of nanolayers, several groups of absorbance can be distinguished. Typical FTIR spectra of one of the samples from type 4_WB_2 are in Fig. 1. In the region around 1900 – 2400 cm^{-1}, spectral distortions are observed due to similar refractive indices of Si containing sample and ATR diamond crystal, lines of this spectral region are not analyzed as bonds of samples. Peaks occurring around 450, 550, 790 and 1150 cm^{-1} are related to Si-O bonds present in the substrate.

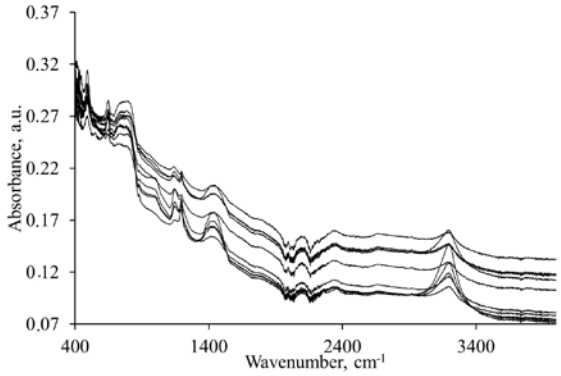

Fig. 1. FTIR spectra of the as-deposited layers, before thermal treatment, of 4_WB_2 sample

Analysis of the FTIR spectra was performed in two steps, starting with comparing the used environments and then continuing with a more detailed analysis of the obtained spectra for the selected thermal treatment environment.

FTIR results for sets of samples thermally treated in various conditions were compared. It is expected, that oxygen in the samples themselves (in SiO_2) together with oxygen added during thermal treatment will oxidize the nanolayers, forming oxides with detectable FTIR signals. As can be seen for example in Fig. 2, samples have relatively broad signals, however, the effect depending on the applied heating conditions can be determined. Samples that have been oxidized in conditions of laboratory air without flow, give the clearest, relatively intense, and interpretable signals – laboratory air without flow signal for around 600 cm^{-1} is more intense and interpretable than the same signal for Ar flow; the signal around 900 cm^{-1} is more intense than laboratory airflow or N_2 flow and the signal at 1150 cm^{-1} is clearer for laboratory air without flow than synthetic air flow. Peaks occurring at 640 cm^{-1}, 860 cm^{-1}, 990 cm^{-1} are related to W-O bonds. In each environment, except laboratory air flow, B-O bond was detected for about 1300 – 1350 cm^{-1} range. Therefore, airflow seems to cause the formation of volatile B containing compounds, while for signals attributing to W oxides, the presence of laboratory air gives the most intense signals. In general, applying flow conditions seem to cause detachment of the layers and subsequently decrease the intensity of FTIR signals. Therefore, as a method of thermal modification of W and WB_2 nanofilms is selected thermal treatment in stationary conditions and further FTIR spectra of non-treated layers (Fig. 3) and thermally treaded layers under no-flow (Fig. 4) are analyzed.

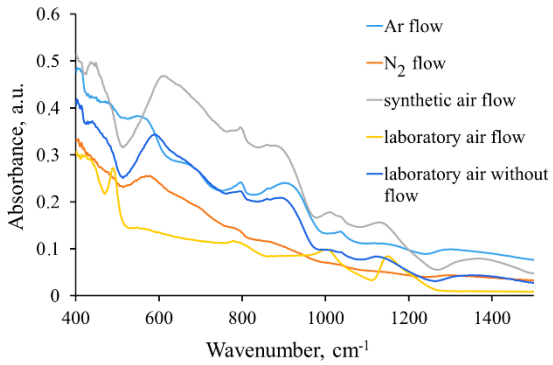

Fig. 2. FTIR spectra of 3_WB_2 samples after thermal treatment under various conditions

FTIR spectra of the as-deposited sample layers showed weak peaks related to Si-O and Si-O-Si bonds, from the SiO_2 substrate. Several new peaks were observed in the spectra of the oxidized layers. The variation in the intensities and the shape of the spectra of thermally non-treated W and WB_2 samples could be due to inhomogeneities of the layers and the thickness of the layer does not play a role in the e.g. intensities of the signals. As can be seen in Fig. 3 b, the variation in spectra is quite large, even considering, that synthesis parameters were the same. As well as for the thermally treated samples both effects need to be considered – oxidation of the surface (W, WB_2) layers as well as temperature caused detachment of the coating and restructuration of the bonds in SiO_2.

Therefore, qualitative analysis of the spectra for both 150 and 200 nm films is selected - positions of the peaks are determined and identified.

For the FTIR spectra recorded for samples treated under the stationary condition in the air (without flow) analysis and decryption of each signal individually is performed. Analysis of signals and their interpretations is shown in Fig. 5. Heating up to 1000 °C seems to cause either delamination of the nanofilms, increasing intensities of Si-O bonds, as well as shows additional oxidation of the substrate. Therefore, 1000 °C is sufficient for complete oxidation of W and B, as well as, involves the participation of the substrate in the reactions. As can be seen from the amount of newly generated bonds, oxidation of the thin films could be used for characterization of their thermal stability (e.g., by applying other heating rates or heating to lower temperatures).

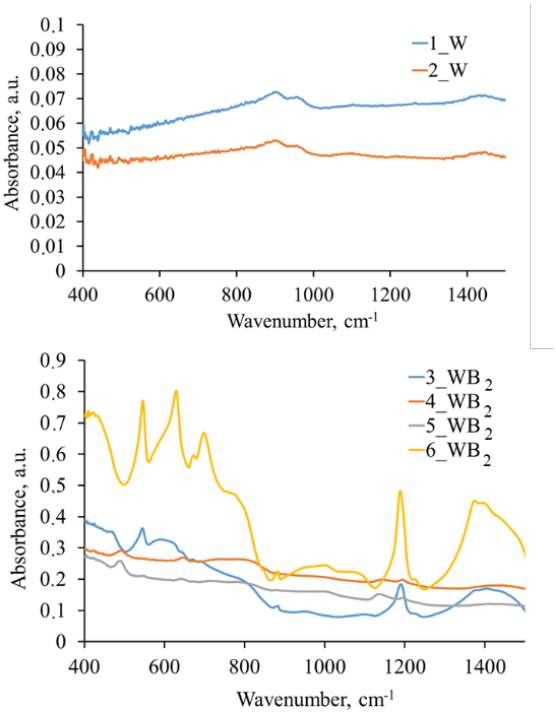

Fig. 3. FTIR spectra of the as-deposited layers before thermal oxidation: W nanolayers and WB_2 nanolayers

The main peaks in the oxidized W layers are at 588, 862 cm^{-1} [12, 17] and are related to W-O. In the boron containing samples, a broad peak about 1300 – 1350 cm^{-1} indicates the presence of BO_3 [24]. Additional peaks in W and WB_2 nanolayer samples observed at 439, 448, 1122, 1151 cm^{-1} [6, 7, 25, 21] correspond to Si-O bonds, and 549, 782, 1011, 1035 cm^{-1} [11, 15, 19, 20] are attributed to Si-O-Si, which may indicate thermally caused delamination of W and WB_2 from the substrate or additional oxidation of Si-SiO_2 substrate if more signals related to Si were observed (Fig. 5). Overall, the newly generated FTIR signals allow to distinguish formation of W-O and W=O bonds, as well as the presence of BO_3 signals in oxidized WB_2 films, allows to apply the abovementioned method for qualitative analysis of synthesized films. It is also observed, that the oxide signal intensities are relatively higher for W samples in comparison with WB_2. In the case of presence of WB_2, the initial intensities are even decreased. It is also visible in Fig. 5., that spectra of 1_W and 2_W samples are with higher intensities.

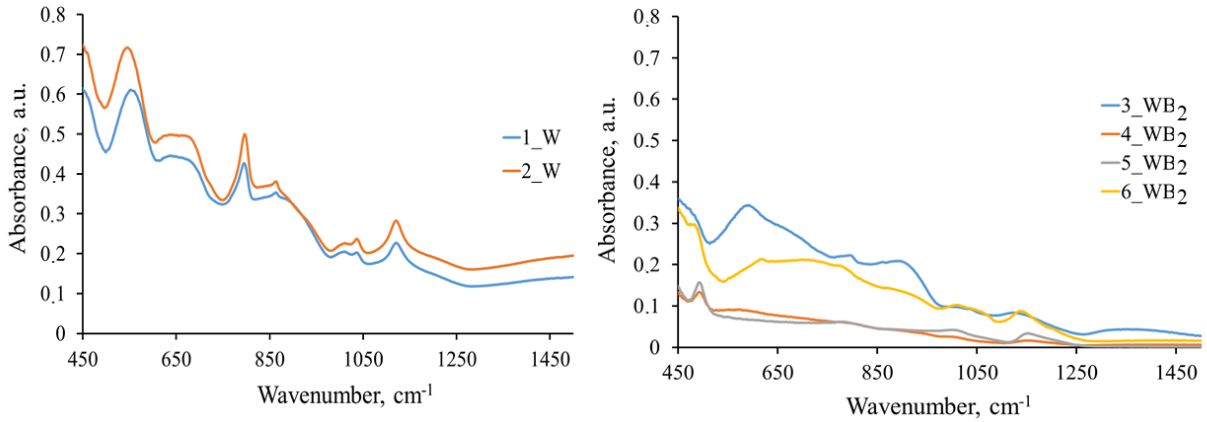

Fig. 4. FTIR spectra of the oxidized layers in laboratory air without flow: W nanolayers and WB_2 nanolayers

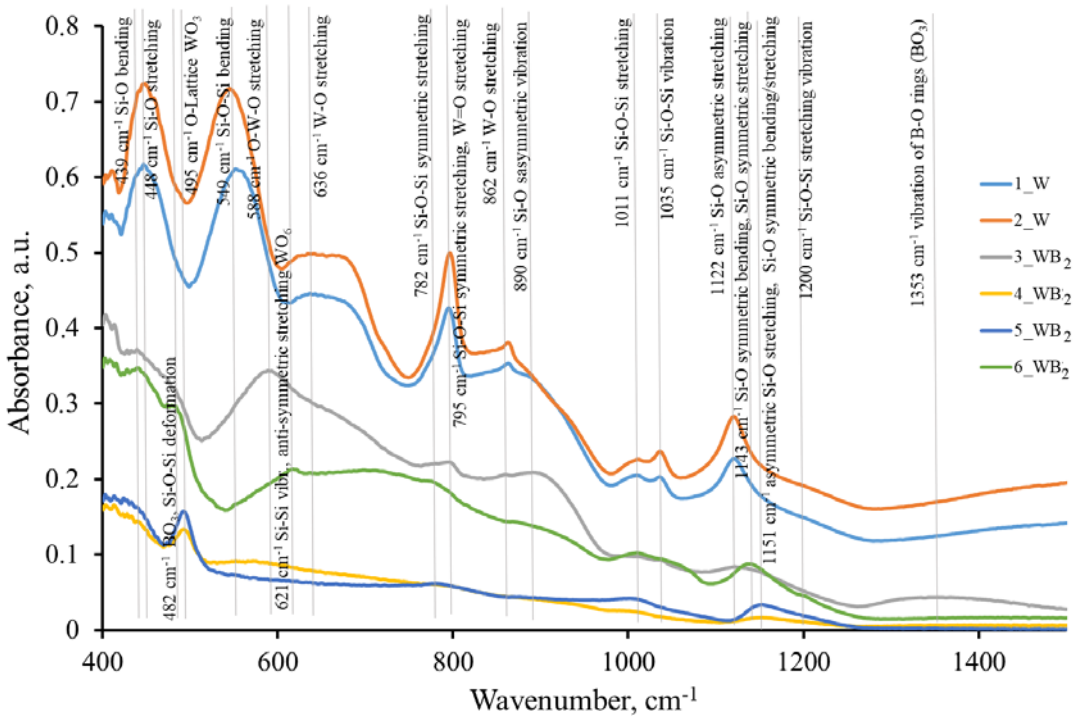

Fig. 5. FTIR spectra of nanolayer samples after thermal oxidation in laboratory air without flow with signal transcripts [6 – 25]

The oxidation method is successfully applied for changing chemical bonds in the synthesized tungsten and tungsten diboride nanolayers. From five applied environments for W and WB_2 of nanolayers, the most intense changes are achieved in laboratory air without flow (stationary conditions), when tungsten and boron oxides are formed and are not detached from the surface by the gas flow. However, by examination 150 and 200 nm of WB_2 no quantitative differences were observed. Therefore, the thermal oxidation method followed by infrared spectrometry can be successfully applied for the qualitative determination of chemical bonds in W and B containing samples. The presence of signals from the oxidized substrate, changes in the signal positions and their intensities gives also information about the thermal stability of the nanofilms and their attachment to the substrate.

4. CONCLUSIONS

The oxidation method can be used to compare W and WB_2 thin film coating on Si-SiO_2 substrate. Heating up to 1000 °C is sufficient for complete oxidation of W and B to achieve the formation of oxides, when can be measured with means of infrared spectrometry. The most intensive changes of signals are achieved by oxidizing thin films in the air in constant conditions (without the flow) in O_2 and H_2O containing air (laboratory air). FTIR spectra of oxidation products show that synthesized films contain W and WB_2 oxidation products. Intensities and the presence of particular bonds can be used for characterization of initial films and their previous elements in composition.

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