

FTIR Analysis of Oxidized Tungsten and Tungsten Diboride Nanolayers

Annija Elizabete GOLDMANE^{1*}, Liga AVOTINA¹, Marina ROMANOVA²,
Alexei MUHIN³, Aleksandrs ZASLAVSKIS³, Gunta KIZANE¹, Yuri DEKHTYAR²

¹ Institute of Chemical Physics, University of Latvia, Jelgavas str.1, Riga, Latvia, LV-1004

² Institute of Biomedical Engineering and Nanotechnologies, Riga Technical University, Kipsalas str.6B, Riga, Latvia, LV-1048

³ Joint-stock company "ALFA RPAR", Ropazu str.140, Riga, Latvia, LV-1006

crossref <http://dx.doi.org/10.5755/j02.ms.29796>

Received 13 September 2021; accepted 02 December 2021

Tungsten (W) and tungsten diboride (WB₂) 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 WB₂ nanofilms with a thickness of 150 nm and 200 nm were deposited on the Si-SiO₂ substrate by the magnetron sputtering technique. The synthesized layers were thermally treated in a thermal analysis device under various gas flow conditions (varying Ar; N₂; synthetic air; air with O₂, N₂, 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 WB₂ layers can be applied for the analysis of W and WB₂ layers on SiO₂ 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 (WB₂) 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 WB₂ can be deposited on dielectrics, such as Si-SiO₂, 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 WB₂ 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 WB₂ 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 WB₂ layers on SiO₂ is necessary.

In this research, the initial W and WB₂ 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 SiO₂ can be developed.

2. EXPERIMENTAL DETAILS

In total, 6 types of samples were studied: 2 coated with W nanolayers and 4 coated with WB₂ nanolayers; sample parameters are given in Table 1.

W and WB₂ layers with a thickness of around 150 nm were deposited at Joint-stock company "ALFA RPAR, the thickness of layers measured with a profilometer.

* Corresponding author. Tel.: +371 670 33937; fax: +371 670 33937.
E-mail address: annija_elizabete.goldmane@lu.lv (A.E. Goldmane)

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-SiO₂ (d = 0.75 μm)

Sample type identifier	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-SiO₂ substrate by the magnetron sputtering technique. Si-SiO₂ substrate was obtained by thermally growing a 0.75 μm thick SiO₂ 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 O₂ 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 ₂ O, CO ₂	~ 45 %
100	Argon	Ar 99.99%	< 5 %
0	Laboratory air	Main components: N ₂ , O ₂ , H ₂ O, CO ₂	~ 45 %

The device is with a horizontal beam balance setup. Sample with mass of around 3 mg placed in Al₂O₃ 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_WB₂ 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.

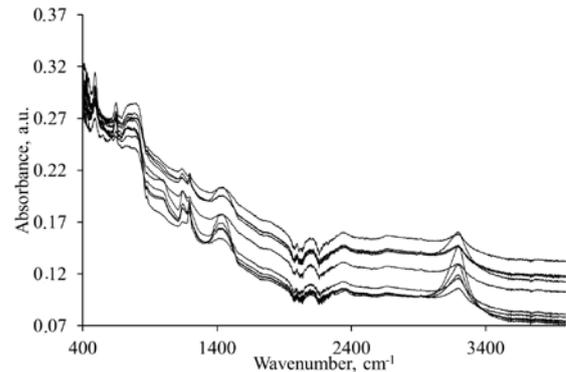


Fig. 1. FTIR spectra of the as-deposited layers, before thermal treatment, of 4_WB₂ sample

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 SiO₂) 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 N₂ 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 WB₂ nanofilms is selected thermal treatment in stationary conditions and further FTIR spectra of non-treated layers (Fig. 3) and thermally treated layers under no-flow (Fig. 4) are analyzed.

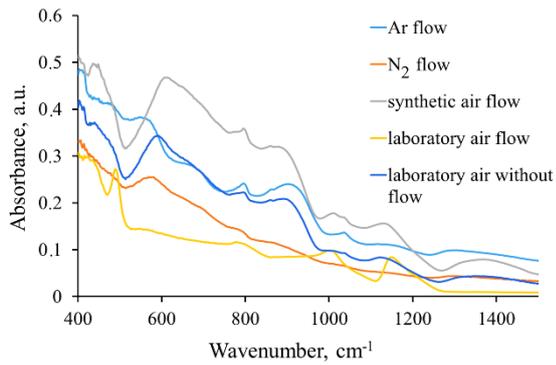


Fig. 2. FTIR spectra of 3_WB₂ samples after thermal treatment under various conditions

FTIR spectra of the as-deposited sample layers showed weak peaks related to Si-O and Si-O-Si bonds, from the SiO₂ 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 WB₂ 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, WB₂) layers as well as temperature caused detachment of the coating and restructuration of the bonds in SiO₂.

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).

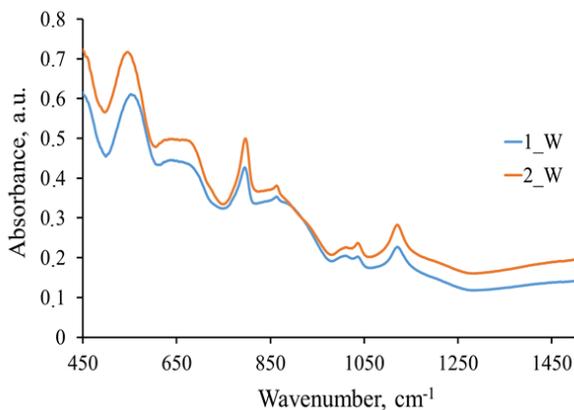


Fig. 4. FTIR spectra of the oxidized layers in laboratory air without flow: W nanolayers and WB₂ nanolayers

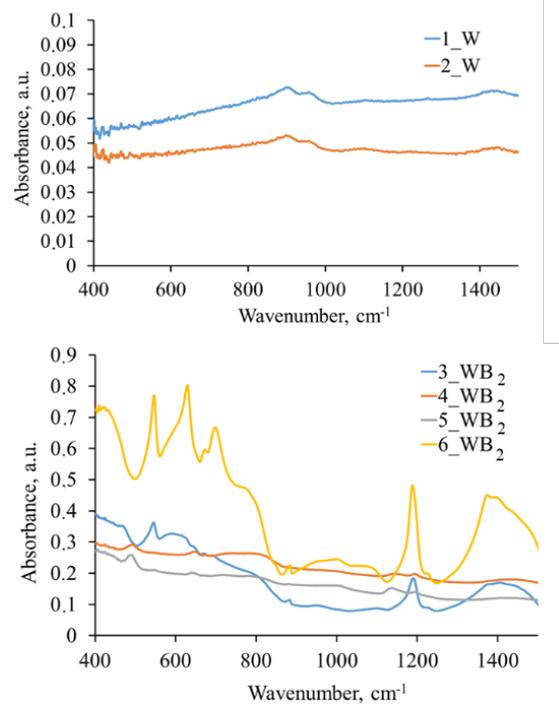
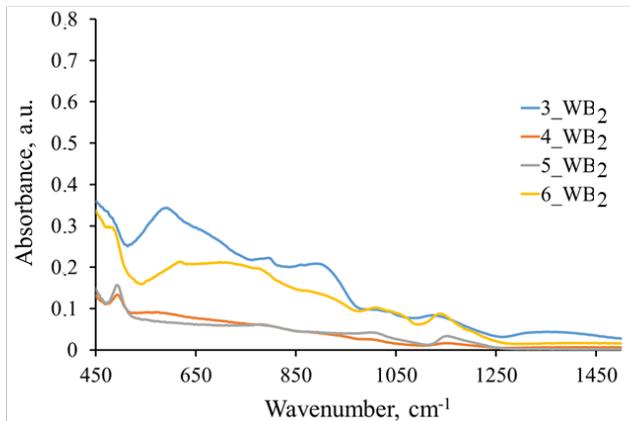


Fig. 3. FTIR spectra of the as-deposited layers before thermal oxidation: W nanolayers and WB₂ nanolayers

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 BO₃ [24]. Additional peaks in W and WB₂ 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 WB₂ from the substrate or additional oxidation of Si-SiO₂ 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 BO₃ signals in oxidized WB₂ 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 WB₂. In the case of presence of WB₂, 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.



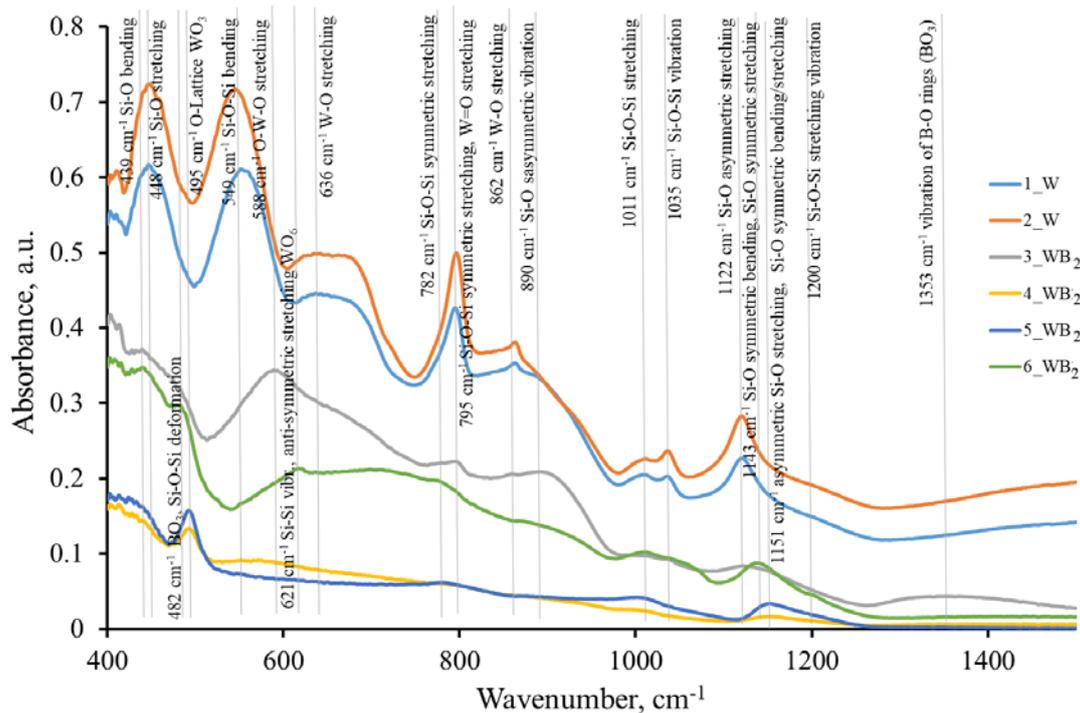


Fig. 5. FTIR spectra of nanolayer samples after thermal oxidation in laboratory air without flow with signal transcripts [6–25]

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 WB₂ 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 WB₂ 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 WB₂ thin film coating on Si-SiO₂ 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 O₂ and H₂O containing air (laboratory air). FTIR spectra of oxidation products show that synthesized films contain W and WB₂ oxidation products. Intensities and the presence of particular bonds can be used for characterization of initial films and their previous elements in composition.

Acknowledgments

The research was supported by the ERDF project No. 1.1.1.1/20/A/109 «Planar field emission microtriode structure» and as well as Project of University of Latvia No. Y5-AZ105-ZF-N-300.

REFERENCES

1. **Gaertner, G.** Historical Development and Future Trends of Vacuum Electronics *Journal of Vacuum Science & Technology B, Nanotechnology and Microelectronics: Materials, Processing, Measurement, and Phenomena* 30 060801 2012: pp. 1–14. <https://doi.org/10.1116/1.4747705>
2. **Demin, G.D., Djuzhev, N.A., Filippov, N.A., Glagolev, P.Y., Evsikov, I.D., Patyukov, N.N.** Comprehensive Analysis of Field-Electron Emission Properties of Nanosized Silicon Blade-Type and Needle-Type Field Emitter *Journal of Vacuum Science & Technology B* 37 022903 2019: pp. 1–7.
3. **Fursey, G.** Field emission in vacuum micro-electronics. *Applied Surface Science, Applied Surface Science* 215 (1–4) 2003: pp. 113–134.
4. **Avotina, L., Pajuste, E., Romanova, M., Enickek, G., Zaslavskis, A., Kinerte, V., Avotins, J., Dekhtyar, Y., Kizane, G.** Surface Morphology of Single and Multi-Layer Silicon Nitride Dielectric Nano-Coatings on Silicon Dioxide and Polycrystalline Silicon *Materials Science (Medžiagotyra)* 26 (1) 2019: pp. 25–29. <https://doi.org/10.5755/j01.ms.26.1.21479>
5. **Burdis, M.S., Siddle John, R., Shona, T.** Fourier Transform Infrared Study of Tungsten Oxide Thin Films and Their Coloration by Lithium *Optical Materials Technology for Energy Efficiency and Solar Energy Conversion XIII SPIE* 2255/371 1994: pp. 371–383. <https://doi.org/10.1117/12.185380>

6. **Zviagina, B.B., Drits, V.A., Dorzhieva, O.V.** Distinguishing Features and Identification Criteria for K-Dioctahedral 1M Micas (Illite-Aluminoceladonite and Illite-Glauconite-Celadonite Series) from Middle-Infrared Spectroscopy Data *Minerals* 10 (2) 153 2020: pp. 1–27. <https://doi.org/10.3390/min10020153>
7. **Shahrokh Abadi, M.H., Delbari, A., Fakoor, Z., Baedi, J.** Effects of Annealing Temperature on Infrared Spectra of SiO₂ Extracted from Rice Husk *Journal of Ceramic Science and Technology* 6 (1) 2014: pp. 41–46. <https://doi.org/10.4416/JCST2014-00028>
8. **Zhang, C.C., Gao, X., Yilmaz, B.** Development of FTIR Spectroscopy Methodology for Characterization of Boron Species in FCC Catalysts *Catalysts* 10 (11) 1327 2020: pp. 1–11. <https://doi.org/10.3390/catal10111327>
9. **Senthil Kumar, R., Rajkumar, P.** Characterization of Minerals in Air Dust Particles in the State of Tamilnadu, India Through FTIR, XRD and SEM Analyses *Infrared Physics & Technology* 67 2014: pp. 30–41. <https://doi.org/10.1016/j.infrared.2014.06.002>
10. **Daniel, M.F., Desbat, B., Lassegues, J.C., Gerand, B., Figlarz, M.** Infrared and Raman Study of WO₃ Tungsten Trioxides and WO₃ · x H₂O Tungsten Trioxide Hydrates *Journal of Solid State Chemistry* 67 (2) 1987: pp. 235–247. [https://doi.org/10.1016/0022-4596\(87\)90359-8](https://doi.org/10.1016/0022-4596(87)90359-8)
11. **Taylor, W.R.** Application of Infrared Spectroscopy to Studies of Silicate Glass Structure: Examples from the Melilite Glasses and the Systems Na₂O-SiO₂ and Na₂O-Al₂O₃-SiO₂ *Journal of Earth System Science* 99 (1) 1990: pp. 99–117. <https://doi.org/10.1007/bf02871899>
12. **Gao, T., Jelle, B.P.** Spectroscopic Properties of Hexagonal Sodium Tungstate Nanorods 2015 IEEE 15th International Conference on Nanotechnology (IEEE-NANO) 2015: pp. 645–648. <https://doi.org/10.1109/nano.2015.7388688>
13. **Young, T., Chen, C., Liou, J.F., Yang, Y.L., Chang, T.C.** Study on the Si–Si Vibrational States of the Near Surface Region of Porous Silicon *Journal of Porous Materials* 7 2000: pp. 339–343. <https://doi.org/10.1023/A:1009622601723>
14. **Boulova, M., Rosman, N., Bouvier, P., Lucazeau, G.** High-Pressure Raman Study of Microcrystalline WO₃ Tungsten Oxide *Journal of Physics- Condensed Matter* 14 (23) 2002: pp. 5849–5863.
15. **Capeletti, L.B., Zimnoch, J.H.** Fourier Transform Infrared and Raman Characterization of Silica-Based Materials *Applications of Molecular Spectroscopy to Current Research in the Chemical and Biological Sciences* 2016: pp. 1–22. <https://doi.org/10.5772/64477>
16. **Pandurangarao, K., Ravi Kumar, V.** Preparation and Characterization of Nanocrystalline Tungsten Oxide Thin Films for Electrochromic Devices: Effect of Deposition Parameters *Materials Today: Proceedings* 2019: pp. 1–8. <https://doi.org/10.1016/j.matpr.2019.10.093>
17. **Usha, K.S., Sivakumar, R., Sanjeeviraja, C., Ichimura, M.** Physical Properties of Rf Magnetron Sputter Deposited NiO:WO₃ Thin Films *Materials Research Express* 2 (1) 016401 2014: pp. 1–14. <https://doi.org/10.1088/2053-1591/2/1/016401>
18. **Saikia, B.J., Parthasarathy, G., Sarmah, N.C.** Fourier Transform Infrared Spectroscopic Characterization of Dergaon H5 Chondrite: Evidence of Aliphatic Organic Compound *Nature and Science* 7 2019: pp. 45–51.
19. **Samah, K.A., Sahar, M.R., Yusop, M.** Structural Properties of Cullet-Paper Ash-Kaolin Clay Ceramic *Journal of Physics: Conference Series* 1083 012007 2018: pp. 1–6. <https://doi.org/10.1088/1742-6596/1083/1/012007>
20. **Lenza, R.F.S., Vasconcelos, W.L.** Structural Evolution of Silica Sols Modified with Formamide *Materials Research* 4 (3) 2001: pp. 175–179. <https://doi.org/10.1590/s1516-14392001000300006>
21. **Yin, Y., Yin, H., Wu, Z., Qi, C., Tian, H., Zhang, W., Hu, Z., Feng, L.** Characterization of Coals and Coal Ashes with High Si Content Using Combined Second-Derivative Infrared Spectroscopy and Raman Spectroscopy *Crystals* 9 (10) 513 2019: pp. 1–12. <https://doi.org/10.3390/cryst9100513>
22. **Mohammadi, M., Khorrami, M.K., Ghasemzadeh, H.** ATR-FTIR Spectroscopy and Chemometric Techniques for Determination of Polymer Solution Viscosity in the Presence of SiO₂ Nanoparticle and Salinity *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 2019: pp. 1–7. <https://doi.org/10.1016/j.saa.2019.04.041>
23. **Alsabah, Y., AlSalhi, M., Elbadawi, A., Mustafa, E.** Synthesis and Study of the Effect of Ba²⁺ Cations Substitution with Sr²⁺ Cations on Structural and Optical Properties of Ba_{2-x}Sr_xZnWO₆ Double Perovskite Oxides (x = 0.00, 0.25, 0.50, 0.75, 1.00) *Materials* 10 (5) 469 2017: pp. 1–12. <https://doi.org/10.3390/ma10050469>
24. **Doweidar, H., El-Damrawi, G., Agammy, E.F.E.** Structural Correlations in BaO–PbO–B₂O₃ Glasses as Inferred from FTIR Spectra *Vibrational Spectroscopy* 73 2014: pp. 90–96. <https://doi.org/10.1016/j.vibspec.2014.05.003>
25. **Saikia, J.** Fourier Transform Infrared Spectroscopic Characterization of Dergaon H5 Chondrite: Evidence of Aliphatic Organic Compound 1,3 Bhaskar *Nature and Science* 7 (5) 2009: pp. 45–51.

