Comparative studies of monoclinic and orthorhombic WO_3 films used for hydrogen sensor fabrication on SiC crystal

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Abstract. Amorphous WO_x films were prepared on the SiC crystal by using two different methods, namely, reactive pulsed laser deposition (RPLD) and reactive deposition by ion sputtering (RDIS). After deposition, the WO_x films were annealed in an air. The RISD film possessed a m-WO_3 structure and consisted of closely packed microcrystals. Localized swelling of the films and micro-hills growth did not destroy dense crystal packing. RPLD film had layered β-WO_3 structure with relatively smooth surface. Smoothness of the films were destroyed by localized swelling and the micro-openings formation was observed. Comparative study of m-WO_3/SiC, Pt/m-WO_3/SiC, and β-WO_3/SiC samples shows that structural characteristics of the WO_3 films strongly influence on the voltage/current response as well as on the rate of current growth during H_2 detection at elevated temperatures.

1. Introduction

Recently, tungsten oxide (WO_3) films have been widely used for the development of resistive and semiconductor sensors of explosive and environmentally harmful gases (Anisimov et al. [1], Trinchi et al. [2], Kandasamy et al. [3], and ets.). For field-effect semiconductor sensors (e.g., metal - metal-oxide - semiconductor, MOS), WO_3 films are deposited on the semiconductor and, as a rule, are coated with a thin film of catalytic metal (Pt, Pd). The use of a silicon carbide (SiC) crystal in such structure provides a significant increase in the operation temperatures, the improved radiation and chemical resistance of sensors. Nakagomi et al. [4], Yamamoto et al. [5] and a number of other authors have demonstrated that WO_3 films can be formed using a variety of the chemical and physical methods. Among the physical vapor deposition methods, reactive pulsed laser deposition (RPLD) and reactive deposition by ion sputtering (RDIS) have certain advantages and they are more often used. Filipescu et al. [6], Fominski et al. [7], and Dellasega et al. [8] have shown that the RPLD of WO_x films exhibits some interesting features influenced by various conditions such as the laser fluence, the reactive/buffer gas pressure, and the post-treatment conditions.

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The aim of this work was to study features of the formation of WO_3 films by using RDIS and RPLD methods for pre-deposition and conventional thermal annealing for post-treatment. It seems important to perform comparative studies of the structure and properties of WO_3 films grown by these methods on the SiC crystal with determination of the factors that have an important effect on the properties of MOSiC sensors for prolonged hydrogen detection at high temperatures.

2. Experimental details

For WO_x films preparation, a 6H-SiC substrate was placed at a distance of 3 cm from a W target in molecular oxygen at a pressure of 5 Pa. In case of RPLD the target was irradiated by nanosecond laser pulses (energy density was ~9 J/cm^2). In case of RDIS a high-voltage pulsed bipolar voltage was applied to the target, which provided W sputtering under ion bombardment, and bombardment of the WO_x film with high-energy ions of gas-discharge plasma. The RDIS WO_3 film was not sensitive enough to H_2, that is why an additional Pt thin film was deposited on the surface of the WO_x film by PLD. After deposition, the films were annealed in air at 550 °C for 1 h. The prepared samples were used for H_2 detection in the range 20–400 °C for more than 1 year.

The prepared samples were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and atomic force microscopy (AFM). Structure of the films was studied by X-ray diffraction method (XRD). To measure current–voltage characteristics (CVCs) of MOSiC samples, the first electrode touched the Pt or WO_3 film surface, while the second one touched the back surface of the SiC substrate, on which an ohmic contact was preliminary obtained by means of Pt deposition and annealing at high temperature. The diameter of the contact area for the probing electrode was no more than 300 μm. The CVCs were measured in air and in air+H_2 (2%) mixture at a temperature of 350 °C.

3. Results and discussion

Post-treatment of the prepared samples in air caused crystallization of as-deposited sub-stoichiometric WO_x films and their chemical composition approached stoichiometric (x~3). Figure 1 shows SEM images of the RDIS WO_3 film covered with Pt on the SiC substrate after annealing post-treatment.

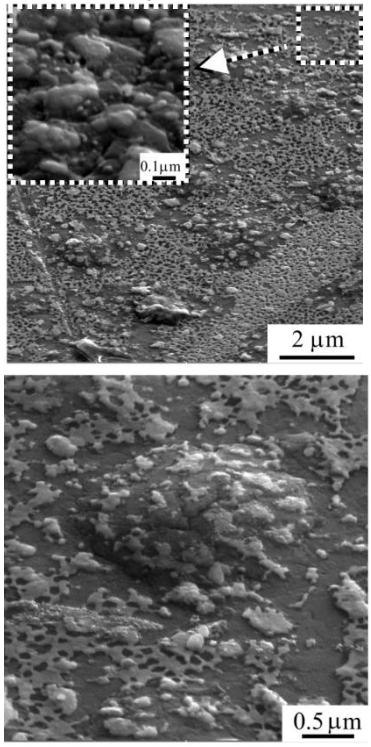

Figure 1. SEM images of

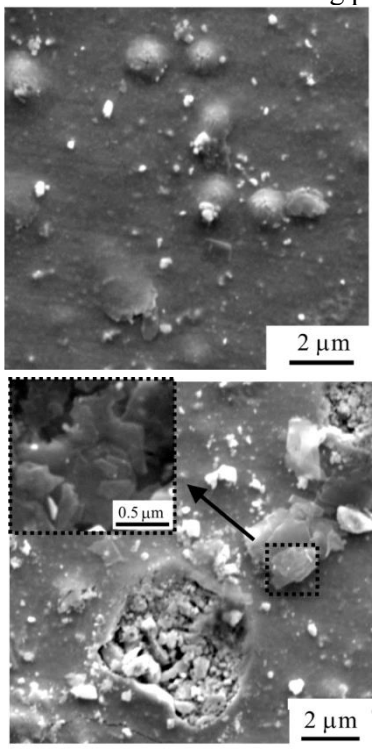

Figure 2. SEM images of

annealed $Pt/WO_3/SiC$ sample prepared by RDIS.

annealed WO_3/SiC sample prepared by RPLD.

The RDIS WO_3 film possessed crystalline structure which consisted of closely packed microcrystals. Localized swelling of the WO_3 films caused the micro-hills (diameter of 2 μm) formation. EDS studies have shown that this process does not destroy dense microcrystal packing (Figure 3). Uniform W and O distributions on the surface of the SiC substrate preserved. Surface of the RDIS films was covered by individual Pt nano-islands. According to XRD measurements, this film contained two monoclinic (m-WO_3) phases (Figure 4).

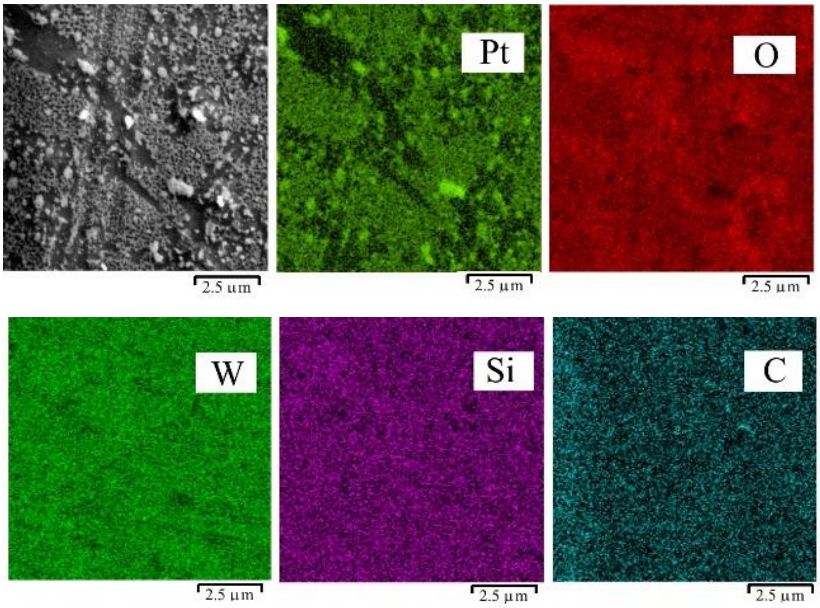

Figure 3. SEM image and EDS maps of the elements for $Pt/WO_3/SiC$ sample.

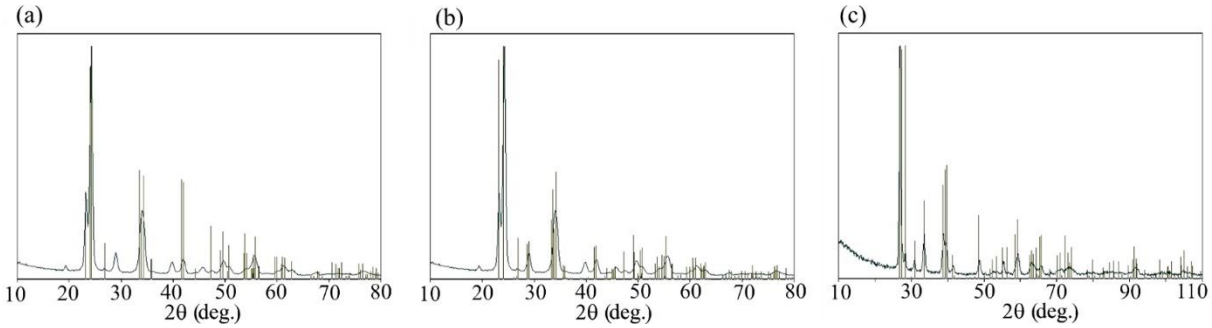

Figure 4. XRD spectra measured for (*a*), (*b*) Pt/m-WO_3/SiC and (*c*) β-WO_3/SiC samples. Tabulated/line spectra for (*a*) monoclinic *mP*16, (*b*) monoclinic *mP*32, and (*c*) orthorhombic *oP*32 phases are shown.

The RPLD WO_3 film possessed relatively smooth surface which was destroyed by localized swelling (Figure 2). Lateral size of the formed hills was ~1 – 7 μm. Large-sized hills could collapse down to SiC substrate and openings appeared in the formed craters. The formation of openings has caused nonuniform distribution of W, O, Si, and C on the EDS maps (Figure 5). There were ~200 micro-openings on an area of 200×200 μm^2. XRD studies have shown (Figure 3) that the RPLD WO_3 film had orthorhombic (β-WO_3) crystal structure with strong texture. For the layered crystalline

structure of β-WO_3, W-containing atomic planes were parallel to each other as well as to the surface of the SiC surface. Such type of atomic layer package resulted in a specific character of film destruction in local areas containing micro-hills. The insert in Figure 2 shows nanosheets that formed due to cracking of the β-WO_3 film. AFM studies of local areas with smooth surface on the RPLD WO_3 film have shown (results not presented) that this film was nanostructured and ~~it~~ consisted of slightly disoriented nanocrystals with sizes ~100 nm.

The character of stationary CVCs has shown that currents are far higher at positive voltage on the Pt or WO_3 contact than at negative. H_2 addition to air resulted in the current increase and the response depended on the temperature and the concentration of H_2. At elevated temperatures (~350 °C), the most distinct response to H_2 from the Pt/m-WO_x/SiC and β-WO_3/SiC samples was achieved at registration of change in voltage/current for the reverse branch of CVCs (Figure 6).

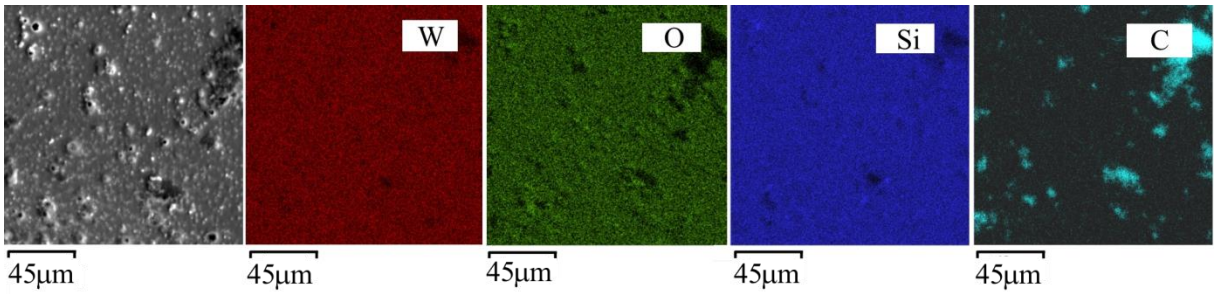

Figure 5. SEM image and EDS maps of elements for the WO_3/SiC sample.

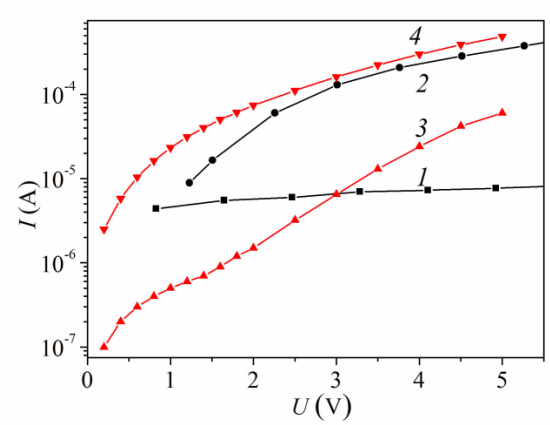

Figure 6. Reverse branches of CVCs for (*1*, *2*) Pt/m-WO_3/SiC and (*3*, *4*) β-WO_3/SiC samples measured (*1*, *3*) in air and (*2*, *4*) in the mixture of air and H_2

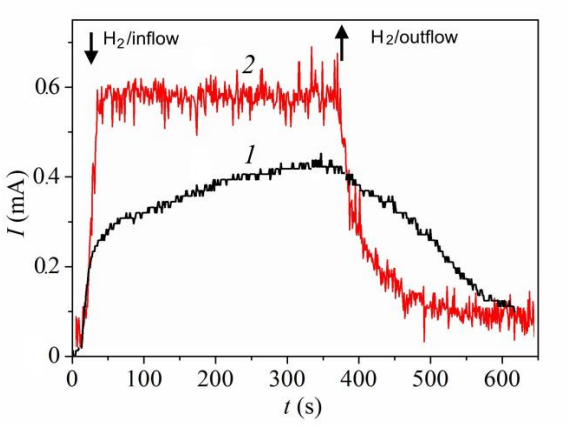

Figure 7. Electric current change on time during inflow and outflow of H_2 for (*1*) Pt/m-WO_3/SiC and (*2*) β-WO_3/SiC samples. Voltage was –5 V; temperature was 350 °C.

For Pt/m-WO_3/SiC sample, the voltage shift of the reverse branch at a current of ~10 μA reached ~5 V. The voltage response of β-WO_3/SiC sample was not so large. However, this sample can effectively detect H_2 without using Pt layer and the current response at a low voltages (< 3 V) was larger than that for Pt/m-WO_x/SiC sample. Moreover, for β-WO_3/SiC sample in comparison with Pt/m-WO_3/SiC sample, the current pulse has grown faster under H_2 inflow and decreased sharply when H_2 was removed (Figure 7). For these samples, the difference in the responses to H_2 may be due to the differences in the structure and morphology of the m-WO_3 and β-WO_3 films. For Pt/m-WO_3/SiC sample, relatively slow kinetics of transport (e.g., diffusion) of atomic hydrogen from the film surface

through the dense m-WO_3 film matrix determines the response of the sensors. The catalytic Pt is necessary for the H_2 dissociation that has not occurred effectively on the m-WO_3 film surface.

For β-WO_3/SiC sample, H_2 transport through openings is possible. In the openings, edges of the nanosheets of the layered β-WO_3 structure could exhibit improved catalytic properties. The layered structure of β-WO_3 film (layers are oriented perpendicular to the axis of openings) facilitates an effective transport into the bulk of β-WO_3 film. At the same time, fast penetration of hydrogen through the openings to the interface between β-WO_3 layer and the SiC substrate could change an energy barrier and initiate the sensor response to H_2.

4. Conclusions

Sensor on MOSiC platform with the compact m-WO_3 film needs the Pt film deposition for activation of H_2 dissociation. The functional layers of Pt/WO_3/SiC sensor preserves solidity and durability and this sensor has larger voltage response. The sensor with the β-WO_3 film has fairly good properties without using Pt and this sensor exhibited obviously enhanced current response and fast response-recovery speed. The sensitivity of the β-WO_3/SiC detector may be caused by unique structural characteristics of the β-WO_3 film consisted of loosely stacked ultra-thin crystalline layers. Such texture of the β-WO_3 film and openings formation in it facilitate H_2 dissociation and effective hydrogen transport. The structure of the β-WO_3 film preserves during prolonged exploitation of the β-WO_3/SiC sensor.

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