Comparative studies of monoclinic and orthorhombic WO$_3$ films used for hydrogen sensor fabrication on SiC crystal

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Abstract. Amorphous WO$_3$ 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$_3$ 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$_3$ 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 $\sim$9 J/cm$^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\sim$3). Figure 1 shows SEM images of the RDIS WO$_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\textsubscript{3}/SiC sample prepared by RDIS.

The RDIS WO\textsubscript{3} film possessed crystalline structure which consisted of closely packed microcrystals. Localized swelling of the WO\textsubscript{3} films caused the micro-hills (diameter of 2 \( \mu \text{m} \)) 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\textsubscript{3}) phases (Figure 4).

![Figure 3. SEM image and EDS maps of the elements for Pt/WO\textsubscript{3}/SiC sample.](image)

![Figure 4. XRD spectra measured for (a), (b) Pt/m-WO\textsubscript{3}/SiC and (c) β-WO\textsubscript{3}/SiC samples. Tabulated/line spectra for (a) monoclinic \textit{mP}16, (b) monoclinic \textit{mP}32, and (c) orthorhombic \textit{oP}32 phases are shown.](image)

The RPLD WO\textsubscript{3} film possessed relatively smooth surface which was destroyed by localized swelling (Figure 2). Lateral size of the formed hills was \( \sim 1 - 7 \mu \text{m} \). 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 \( \sim 200 \) micro-openings on an area of 200\( \times \)200 \( \mu \text{m}^2 \). XRD studies have shown (Figure 3) that the RPLD WO\textsubscript{3} film had orthorhombic (β-WO\textsubscript{3}) crystal structure with strong texture. For the layered crystalline
structure of β-WO₃, 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-WO₃ film. AFM studies of local areas with smooth surface on the RPLD WO₃ film have shown (results not presented) that this film was nanostructured and 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 WO₃ contact than at negative. H₂ addition to air resulted in the current increase and the response depended on the temperature and the concentration of H₂. At elevated temperatures (~350 °C), the most distinct response to H₂ from the Pt/m-WOₓ/SiC and β-WO₃/SiC samples was achieved at registration of change in voltage/current for the reverse branch of CVCs (Figure 6).

For Pt/m-WOₓ/SiC sample, the voltage shift of the reverse branch at a current of ~10 μA reached ~5 V. The voltage response of β-WO₃/SiC sample was not so large. However, this sample can effectively detect H₂ without using Pt layer and the current response at a low voltages (< 3 V) was larger than that for Pt/m-WOₓ/SiC sample. Moreover, for β-WO₃/SiC sample in comparison with Pt/m-WOₓ/SiC sample, the current pulse has grown faster under H₂ inflow and decreased sharply when H₂ was removed (Figure 7). For these samples, the difference in the responses to H₂ may be due to the differences in the structure and morphology of the m-WOₓ and β-WO₃ films. For Pt/m-WOₓ/SiC sample, relatively slow kinetics of transport (e.g., diffusion) of atomic hydrogen from the film surface.
through the dense m-WO₃ film matrix determines the response of the sensors. The catalytic Pt is necessary for the H₂ dissociation that has not occurred effectively on the m-WO₃ film surface.

For β-WO₃/SiC sample, H₂ transport through openings is possible. In the openings, edges of the nanosheets of the layered β-WO₃ structure could exhibit improved catalytic properties. The layered structure of β-WO₃ film (layers are oriented perpendicular to the axis of openings) facilitates an effective transport into the bulk of β-WO₃ film. At the same time, fast penetration of hydrogen through the openings to the interface between β-WO₃ layer and the SiC substrate could change an energy barrier and initiate the sensor response to H₂.

4. Conclusions

Sensor on MOSiC platform with the compact m-WO₃ film needs the Pt film deposition for activation of H₂ dissociation. The functional layers of Pt/WO₃/SiC sensor preserves solidity and durability and this sensor has larger voltage response. The sensor with the β-WO₃ 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-WO₃/SiC detector may be caused by unique structural characteristics of the β-WO₃ film consisted of loosely stacked ultra-thin crystalline layers. Such texture of the β-WO₃ film and openings formation in it facilitate H₂ dissociation and effective hydrogen transport. The structure of the β-WO₃ film preserves during prolonged exploitation of the β-WO₃/SiC sensor.

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