



Effect of substrate structures on epitaxial growth and electrical properties of WO₃ thin films deposited on ($\bar{1}012$) and (0001) α -Al₂O₃ surfaces

Ahmad Al Mohammad*

Nano-Materials Labs, Physics Department, Atomic Energy Commission of Syria, 17th Nissan Street, P.O. Box 6091, Damascus, Syrian Arab Republic

ARTICLE INFO

Article history:

Received 3 December 2008

Received in revised form

7 April 2009

Accepted 8 April 2009

Keywords:

WO₃ thin film

RHEED

Gas sensor

Epitaxial growth

Electrical conductivity

ABSTRACT

The effect of surface structures of annealed ($\bar{1}012$) and (0001) α -Al₂O₃ substrates on epitaxial growth and electrical properties of electron beam deposited WO₃ thin films has been investigated. (0001) and ($\bar{1}012$) α -Al₂O₃ surfaces were used in (1 × 1) stoichiometric and reconstructed forms. The structure and the morphology of WO₃ films were determined by transmission electron microscopy (TEM), selected area electron diffraction (SAED) and reflection high energy electron diffraction (RHEED). Generally the films consist of micro-grains of monoclinic WO₃ and the (010) planes are parallel to the substrate surfaces. Certain epitaxial relationships between WO₃ films and the substrate surfaces were found. These phenomena are interpreted by nucleation and growth theories in relation to a variation of the density of surface oxygen vacancies of the α -Al₂O₃ substrates. The electrical conductivity of the WO₃ films was measured as a function of annealed temperatures of the substrates. The activation energy for conduction deduced from the Arrhenius equation is found to be dependent on the grain size and the morphology of WO₃ films.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Tungsten oxide (WO₃) films have been widely studied and used in many applications such as electro-optical, electro-chromic, ferroelectric and gas sensors [1–3]. The growth behavior of WO₃ films on the α -Al₂O₃ substrates was studied using several techniques such as molecular beam epitaxy, reactive radio-frequency (RF) magnetron sputtering and thermal evaporation [3–6]. Knowing the growth behavior of WO₃ is helpful for the fabrication of high quality WO₃ thin films [7]. In our previous reports, we focused on the effect of surface structure of substrates on controlling the growth parameters of the WO₃ films [5,8]. We found that the surface structure of α -Al₂O₃ substrates determined the properties of WO₃ films such as the crystallographic structures, the electrical conductivities, gas sensing and optical properties [8–14]. It has been shown [14–16] that the increasing of temperature during thermal treatments of α -Al₂O₃ substrates under vacuum reduced their surface structures. It led to the formation of a thin aluminum-rich layer giving the excitation of aluminum surface plasmons on α -Al₂O₃ surfaces. The surface structures are typically deduced from low energy electron diffraction (LEED) and reflection high energy electron diffraction (RHEED) experiments. The

reconstruction of clean α -Al₂O₃ surfaces heated at high temperature has been reported including a ($\sqrt{31} \times \sqrt{31}R9^\circ$) surface structure of the (0001) substrates. (2 × 1) and (2 × 2) surface structures have been observed by LEED on the ($\bar{1}012$) surface. All the observations were performed after annealing in vacuum [14,15].

In this work, we investigated the morphology and the epitaxial growth of WO₃ films on the ($\bar{1}012$) and (0001) α -Al₂O₃ surfaces by means of transmission electron microscope (TEM), selected area electron diffraction (SAED) and RHEED. The electrical conductivity of WO₃ films prepared on different surface structures of α -Al₂O₃ substrates was measured to relate the conductivity mechanisms to the structure and morphology of WO₃ films.

2. Experimental

The substrates consisted of thin slides of α -Al₂O₃, cut from an alumina single crystal. The slides were mechanically and chemically polished so that the (0001) or ($\bar{1}012$) planes were parallel to the surface. Prior to the evaporation, the α -Al₂O₃ substrates were heated at either 1100 K for stoichiometric substrates or 2000 K for reconstructed ones. All substrates were heated for 3 h under a vacuum of about 10⁻³ Pa. Their surface structures were examined by RHEED (Elettrorava, Italy), and atomic force microscopy, AFM (Autoprobe CP, Park Scientific Instruments, USA). The tungsten oxide thin films were electron beam deposited (EBD) using a commercial system (Elettrorava, Italy) simultaneously on all the

* Tel.: +963 11 2132580; fax: +963 11 6112289.

E-mail addresses: scientific@aec.org.sy, aalmohammad@aec.org.sy

substrates which were placed near one to other on the same heating support and under a residual O_2 pressure about 5×10^{-1} Pa. The WO_3 powder (Aldrich, $\sim 20 \mu$, 99+% purity) was compressed in discs of 5 mm and annealed in an oxygen atmosphere at 1000 K for 1 h before using in the crucible of electron gun. During the WO_3 deposition, the α - Al_2O_3 substrates were maintained at a deposition temperature $T_d = 575$ K. The vapor flow corresponds to a deposition rate of approximately 2 nm/min and the average thickness deposited is approximately 40 nm. The structure and morphology of thin films were studied by RHEED. Some films were then detached from their substrates in hydrofluoric acid to be examined ex-situ by TEM (Siemens102, A.V. is 125 KV). The conductivity is calculated from the experimentally determined resistance R , which is monitored during the three heating and cooling cycles. The heating cycles are carried out in a residual pressure of oxygen about 10 Pa for temperature at 623 K.

3. Results

The (0001) and $(\bar{1}012)$ surfaces of α - Al_2O_3 have been chosen for their completely different crystallographic properties, which can be seen in Fig. 1. The (0001) surface is a basal plane of a hexagonal alumina lattice due to the -Al-O-Al-O- crystal structure. It can be formed by close-packed hexagonal O planes, if the crystal is ending by oxygen layer. If the upper plane is the aluminum one, the surface is formed by Al atoms lying on trigonal oxygen sites. The $(\bar{1}012)$ surface is the more stable crystallographic plane and consists of two atomic layers. The first is centered rectangular structure cutting the Al and O crystal layers. The second is formed by zigzag lines parallel of only oxygen atoms. Before the deposition of WO_3 films the α - Al_2O_3 surfaces were examined by RHEED and AFM methods, Fig. 2. The azimuth directions of incidence RHEED electron beam on surfaces were registered. The SAED and the RHEED patterns of WO_3 deposited films on all substrates exhibit a monoclinic crystallographic structure (P21/n space group of WO_3) with lattice parameters: $a = 7.311(4) \text{ \AA}$, $b = 7.542(6) \text{ \AA}$, $c = 7.691(6) \text{ \AA}$, $\beta(a, c) = 90^\circ 88'$. Fig. 3 is an example of the TEM micrographs and the SAED patterns obtained from deposited WO_3 thin films. These micrographs show regular shaped grains on substrates while the mean grain size varies from substrate to another. In all cases, the SAED patterns confirm that the films have a monoclinic structure with (010) planes, which are parallel to the substrate surfaces. We have achieved a more accurate estimation of the film structure and epitaxial relationships between WO_3 films and α - Al_2O_3 substrates by RHEED investigations. In general, the deposition of the WO_3 films results in electron diffraction patterns with well defined elongated reflections perpendicular to the shadow line. The reflection lines are of 00l, -201 and -101 types due to large monocrystalline domains with the (010) plane parallel

to surface. These patterns are interpreted from the monoclinic structure of WO_3 . Fig. 4 represents the principal RHEED patterns of the WO_3 films on the different α - Al_2O_3 substrates and the corresponding theoretical interpretation of these patterns. We deduce that the WO_3 films on all substrates consist of one or two domains whose surfaces are parallel to the (010) plane. Hence the WO_3 films are formed of monocrystalline domains in epitaxy on the α - Al_2O_3 supports according to the certain relationships. The main results of the investigations of the TEM micrographs and the RHEED and the SAED patterns are reported in Table 1.

Fig. 5 displays the conductivity σ of the WO_3 films deposited on stoichiometric and reconstructed α - Al_2O_3 substrates as a function of the reciprocal temperature (in a $\text{Log } \sigma$ versus $10^3/T$ plot). We have observed for these conditions that during the heating or cooling cycles, the values of conductivity have very small variations which are attributed to experimental errors. Generally the observed conductivity of the WO_3 films on different α - Al_2O_3 substrates suggests polycrystalline n-type semiconductor behavior.

4. Discussion

The results concern the growth of WO_3 films on (0001) and $(\bar{1}012)$ α - Al_2O_3 surfaces carried out under the same deposition conditions exhibit different crystallographic structure resulting from thermal annealing of the α - Al_2O_3 substrates. In case of $(\bar{1}012)$ surfaces, the annealing produces reconstructed (1×2) surface with large number of oxygen vacancies, which are surface defects. Generally these oxygen vacancies can be considered as nucleation sites. This fact supports the hypothesis that the difference in nucleation density is due to defects created by annealing. While the annealing of (0001) surface gives one or more (111) aluminum layers on the surface, which is responsible for changes in growth mode of WO_3 films. The crystallographic and morphologic properties of WO_3 films, which are grown on reconstructed (0001) surface, are resulting from Frank-Van der Merwe (layer-by-layer) growth mode. The WO_3 films, which grown on other kinds of substrates, are resulting from Volmer-Weber (islands or 3D growth) mode.

It is possible by the RHEED and the SAED methods to explore the various orientations of the WO_3 film by rotating the sample in its plane or tilting the substrates' holders which change the azimuth directions of the electron beam. These changes could provide an important information about the reciprocal lattice of the WO_3 films. The most important crystallographic properties are crystal symmetry and in-plane lattice constant. Although the two-dimensional (2D) symmetry of the substrate surface is the most important, the three-dimensional (3D) symmetry can also be influential in determining the structure of the interface layer, especially for oxide-on-oxide epitaxial growth. It has been found that the minimization of electrostatic repulsion within a few

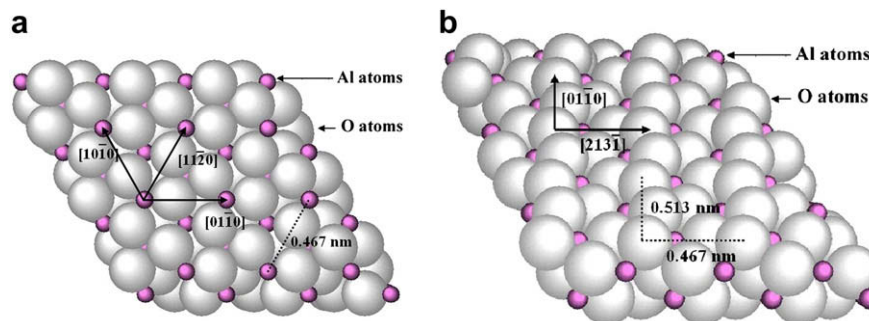


Fig. 1. (a) The (0001) α - Al_2O_3 plane with the crystallographic directions and the distance between the surface aluminum atoms, (b) the $(\bar{1}012)$ α - Al_2O_3 plane with the crystallographic directions and the distances between the surface oxygen atoms.

Download English Version:

<https://daneshyari.com/en/article/1689592>

Download Persian Version:

<https://daneshyari.com/article/1689592>

[Daneshyari.com](https://daneshyari.com)