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Conductivity in transparent anatase TiO_2 films epitaxially grown by reactive sputtering deposition

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Abstract

The synthesis of semiconducting TiO_2 thin films deposited by reactive sputtering is discussed. In particular, defect doping of the anatase polymorph that is epitaxial stabilized on (0 0 1) $LaAlO_3$ was explored using either oxygen or water vapor as the oxidizing species. For films grown in oxygen, a transition from insulating to metallic conductivity of the films is observed as the O_2 pressure is reduced. X-ray diffraction measurements show the presence of the Ti_nO_{2n-1} phase when the oxygen pressure is reduced sufficiently to induce conductive behavior. Hall measurements indicate that these materials are p-type. In contrast, the use of water vapor as the oxidizing species enabled the formation of n-type semiconducting TiO_2 with carrier density on the order of 10^{18} cm^{-3} and mobility of 10–15 $cm^2/V\,s$.

In recent years, there has emerged significant interest in the synthesis of semiconducting TiO_2 thin films. TiO_2 is a wide bandgap oxide that occurs in three distinct polymorphs, namely rutile, anatase, and brookite. Undoped anatase is an anisotropic, tetragonal insulator ($a = 3.78$ Å, $c = 9.52$ Å) with a bandgap of 3.2 eV [1]. Rutile exhibits a gap of ~3.0 eV. It has been reported that TiO_2 can be made an n-type semiconductor with $n \sim 10^{19}$ cm^{-3} via chemical substitution or by Ti interstitials [2–5]. Low temperature electron Hall mobility on the order of 30–100 $cm^2/V\,s$ has been reported for rutile. Hall mobility of electron-doped anatase has been measured as high as 20 $cm^2/V\,s$. Recently, interest in semiconducting TiO_2 has shifted to transition metal doped materials. Experiments have shown that Co-doped TiO_2 is a dilute magnetic semiconductor with a Curie temperature well above room temperature [6]. The mechanism by which ferromagnetism occurs in this doped semiconductor system is assumed to be carrier mediated. As such, a key issue in exploiting TiO_2 for spintronic applications is to understand the film growth conditions that yield mobile carriers in the TiO_2 matrix.

The focus of this paper is on the synthesis and properties of semiconducting TiO_2. In particular, we have investigated the transport properties of sputter-deposited TiO_2 films using either O_2 or H_2O as the oxidizing species. Here, we address the issues of phase development, crystallinity, conductivity, and surface morphology of TiO_2 as a function of oxidizing species, oxidation conditions, and temperature using reactive sputter deposition.

The film growth experiments were performed in a reactive RF magnetron sputter deposition system equipped with a load-lock for substrate exchange. A quartz lamp heater provided for substrate heating up to 750 °C. Two-inch diameter Ti sputtering targets were used. The target to substrate distance was approximately 15 cm. The base pressure of the deposition system was on the order of 5×10^{-8} Torr. For epitaxially stabilized anatase film growth, (0 0 1) $LaAlO_3$ was chosen as the substrate as it provides a lattice mismatch on the order of 0.2% with anatase. Anatase is a metastable polymorph that can be realized in polycrystalline films

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deposited at low temperatures [7–11]. Rutile is the thermodynamically stable TiO_2 phase at high temperatures, and is the most widely studied. In general, epitaxial stabilization offers a means by which anatase thin films can be obtained on lattice-matched substrates, often for processing conditions where the phase is thermodynamically unstable in bulk. Numerous efforts have also focused on the formation of epitaxial anatase films that are phase pure and highly crystalline [12–22].

The substrates were cleaned in trichloroethylene, acetone, and ethanol prior to mounting on the sample platen with Ag paint. Oxygen was provided through a mass flow control valve. A water source was created by freezing and evacuating a water-filled stainless steel cylinder that was attached to the deposition chamber via a leak valve. Upon returning to room temperature, the vapor pressure of water is sufficient to provide an H_2O source. Previous work reporting highly crystalline anatase films via reactive sputter deposition focused on the phase development of TiO_2 when oxygen or H_2O are used as the oxidant [23]. The introduction of the hydrogen-bearing species into the growth process provides the potential of modifying the Ti valence state in the TiO_2 matrix.

For the experiments focusing on the growth of TiO_2 using oxygen as the oxidizing species, films were deposited at substrate temperatures ranging from 400 to 700 °C in an oxygen ambient of 10^{-2} to 10^{-4} Torr. The total pressure was 15 mTorr for most experiments. Over this range of conditions, the formation of semiconducting TiO_2 was not observed. Instead, a transition from insulating TiO_2 to metallic films, with Ti_nO_{2n-1} as a secondary phase was observed as the oxygen partial pressure was reduced. Fig. 1 shows a compilation of sputtering conditions in which the transport properties are characterized as a function of O_2 and Ar pressure. The films shown were grown at 700 °C. The most significant parameter in determining transport properties is

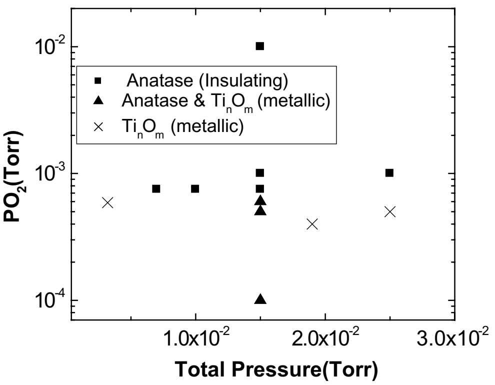

Fig. 1. Phase map showing crystalline phases and conductivity behavior as a function of deposition conditions.

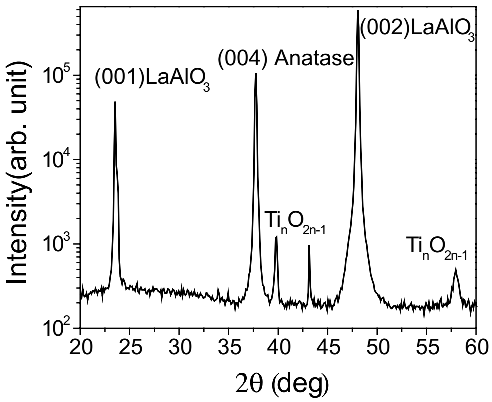

Fig. 2. X-ray diffraction patterns for Ti–O film deposited at an Ar pressure of 15 mTorr and an oxygen partial pressure of 10^{-4} Torr on $LaAlO_3$ at 700 °C, showing the presence of both anatase and Ti_nO_{2n-1}.

oxygen pressure as this determines the formation of defects in the TiO_2 matrix that leads to conducting behavior. For growth at $P(O_2) \geqslant 7.5\times10^{-4}$ Torr, the films are insulating and transparent. For $P(O_2) \leqslant 7.5\times10^{-4}$ Torr, the films become conductive and black. Both the X-ray diffraction data and Hall measurements indicate that the observed conductivity is not due to defect-doped anatase or rutile, but due to a metallic Ti_nO_{2n-1} impurity phase. Ti_nO_{2n-1} phases, such as Ti_4O_7, are metallic at room temperature. Fig. 2 shows the X-ray diffraction pattern for a Ti–O film grown at 700 °C, $P(O_2) = 10^{-4}$ Torr, $P_{Ar} = 15$ mTorr. The diffraction data shows both TiO_2 anatase and Ti_nO_{2n-1} peaks. In addition, the Hall measurements indicate that these films are metallic and p-type. The Hall measurements yield a carrier density on the order of 10^{23} cm^{-3}, a resistivity of 7×10^{-5} Ωcm, and a mobility of 0.36 cm^2/V s. Fig. 3 shows the results from Hall measurements for the films grown at a $P(O_2) \leqslant 10^{-3}$ Torr. In all cases, the Hall voltage sign is positive, indicating p-type conductivity.

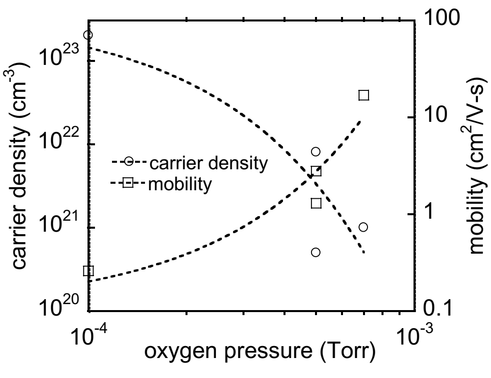

Fig. 3. Hall data for TiO_2 films grown at 700 °C in oxygen.

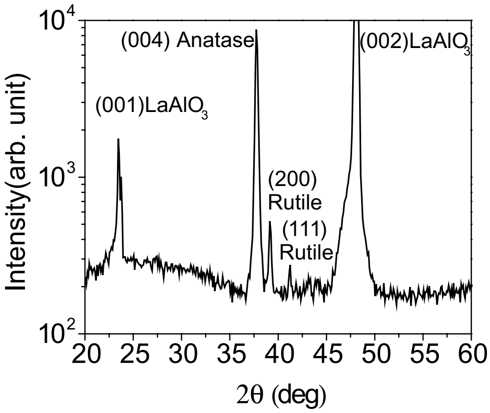

Fig. 4. X-ray diffraction data for TiO_2 on $LaAlO_3$ using H_2O.

For films grown at $P(O_2) \geqslant 10^{-3}$ Torr, the films are insulating. This metal–insulator transition seen in the transport with varying oxygen during growth corresponds to the appearance of Ti_nO_{2n-1} as a second phase in the TiO_2 matrix.

We have also examined the use of H_2O as the oxidizing species in synthesizing TiO_2 thin films. Previous work showed that phase-pure anatase films could be realized using water vapor as the oxidant. In contrast to the case of O_2, processing conditions are identified in which n-type semiconducting films can be realized. For films grown at 600–650 °C in 10^{-3} Torr H_2O, the films are transparent, n-type, and exhibit no Ti_nO_{2n-1} peaks in the X-ray diffraction patterns. Fig. 4 shows the X-ray diffraction pattern for a TiO_2 film grown at 650 °C in 10^{-3} Torr H_2O. Note that the strongest peaks can be assigned to anatase with a much smaller peak corresponding to rutile. Table 1 lists the specific properties of films grown under these conditions. Deposition at 10^{-4} Torr H_2O yielded Ti_nO_{2n-1} peaks and metallic behavior.

In addition to transport and structural properties, film morphology for TiO_2 grown using H_2O was examined using atomic force microscopy (AFM). Fig. 5 shows the AFM images of TiO_2 films grown in $P(H_2O)$ 10^{-3} Torr at various substrate temperatures. Two items should be noted. First, the grain size increases significantly as the growth temperature is increased from 550 to 750 °C. The average grain size for films grown at 550 °C is on the order of 80 nm. At 750 °C, the grain size is on the order of 250 nm. With this increase in grain size,

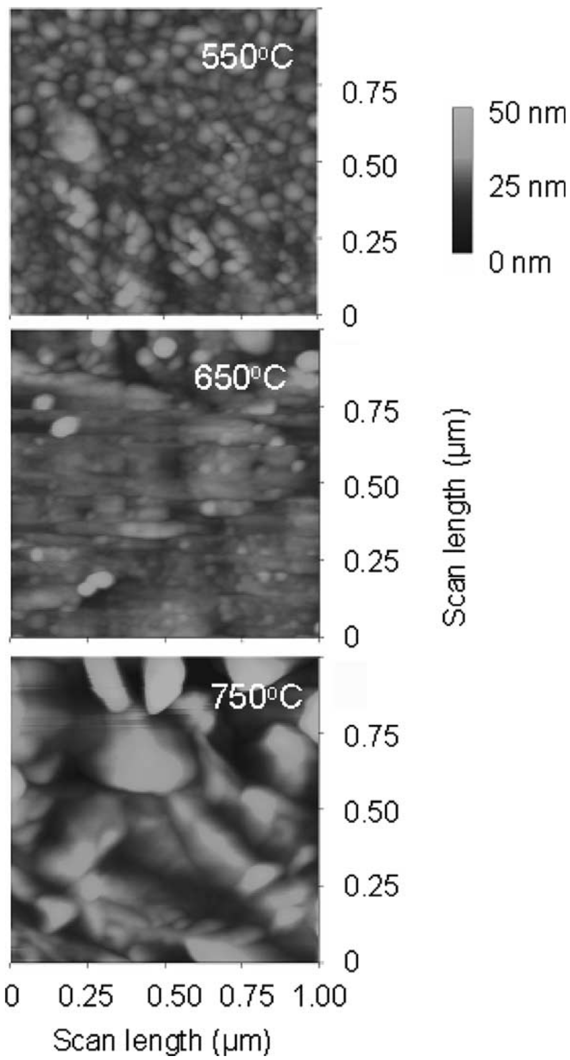

Fig. 5. Atomic force microscope scan of anatase film grown in water vapor at different temperatures.

an increase in RMS roughness is also observed, increasing from 3.1 nm at 550 °C to 9.3 nm at 750 °C.

In conclusion, we have investigated the synthesis of semiconducting TiO_2 possessing the anatase structure on (0 0 1) $LaAlO_3$ using reactive sputter deposition. Phase-pure anatase could be achieved using either water vapor or oxygen as the oxidizing species, although n-type semiconducting behavior was observed only with the use

Table 1
Deposition conditions and semiconducting properties of TiO_{2-x} films deposited using water vapor

Growth temperature (°C)	P_{H_2O} (Torr)	Carrier type	n (cm^{-3})	ρ (Ω cm)	μ_{Hall} (cm^2/V s)
650 °C	10^{-3}	n	2×10^{18}	0.29	13
600 °C	10^{-3}	n	2.5×10^{18}	3	0.7

of water vapor. Future activities will focus on understanding the electronic, doping, and optical properties of these films when doped with transition metals, such as Co.

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