Epitaxial Growth, Doping, and Electron Transport of the Semiconducting Oxides
In$_2$O$_3$, Ga$_2$O$_3$, and SnO$_2$

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Abstract

The growth of high-quality, single-crystalline SnO$_2$, In$_2$O$_3$, and Ga$_2$O$_3$ films by plasma assisted molecular beam epitaxy is presented. The growth-related issues faceting, nucleation, and sub-oxide formation are discussed. The resistivity of SnO$_2$ and In$_2$O$_3$ was systematically varied from semi-insulating to highly conductive behavior by donor and (deep)acceptor doping. Realization of p-type conductivity seems to be hard or impossible. The influence of the surface electron accumulation layer on conductivity, its control, and its impact on contacts will be described. With the example of In$_2$O$_3$ the influence of intrinsic defects on transport properties will be demonstrated.

1. Introduction

Semiconducting oxides are playing a growing role as active device material in (opto)electronic devices. Application in transparent electronic devices, power electronics, or photo-detectors requires a semiconductor-like material quality in contrast to the low material quality sufficient for the conventional transparent contact applications of these oxides.

This study investigates the growth of high-quality semiconducting oxide layers, their conductivity and its control, and their contact and transport properties relevant for device applications.

2. Experiment

Plasma assisted molecular beam epitaxy (PAMBE) was used to grow SnO$_2$, In$_2$O$_3$, and Ga$_2$O$_3$ layers with high crystal quality and purity, and with well-defined transport properties by systematic donor and (deep) acceptor doping [1]. Resistivity, Hall, and Seebeck coefficient measurements were used to investigate the transport properties of the grown films. Annealing in different atmospheres was used to alter the (compensating) intrinsic defect concentration in In$_2$O$_3$. Current-voltage measurements with different contact metals were used to investigate contact properties, and XPS measurements identified the presence/absence of surface accumulation layers. Surface treatments with an oxygen plasma helped depleting the surface accumulation.

3. Results and discussion

3.1 Growth

Due to the absence of native substrates, growth was performed by heteroepitaxy on foreign substrates, i.e. r-plane Al$_2$O$_3$ for single crystalline rutile SnO$_2$(101) and ZrO$_2$:Y(001) [YSZ(001)] for single crystalline cubic In$_2$O$_3$(001). Ga$_2$O$_3$ was grown on c-plane Al$_2$O$_3$ (with rotational domains) and on single crystalline on beta-Ga$_2$O$_3$(100). The recent availability of native oxide substrates for all semiconducting oxides investigated in this work will lead to a further variation in crystal quality. The formation and sublimation of volatile, parasitic suboxides for SnO$_2$ [2] and Ga$_2$O$_3$ [3] results in a decreasing growth rate in the metal-rich growth regime. For In$_2$O$_3$, the anisotropy of the surface free energy leads to the preferential formation of {111}-facetted surfaces for the growth of (001)-oriented In$_2$O$_3$ (Fig.1, top), whereas (111)-oriented In$_2$O$_3$ formed smooth surfaces. Metal-rich growth conditions were able to lower the In$_2$O$_3$ (001) surface free energy enabling the growth of smooth, unfacetted In$_2$O$_3$ (001) layers (Fig.1, bottom) [4].

Fig. 1 Morphology of In$_2$O$_3$ films grown on YSZ(001) under oxygen-rich conditions (top) and indium-rich conditions (bottom).
In$_2$O$_3$ grows in a Volmer-Weber growth mode on YSZ(001), resulting in suppressed nucleation on the substrate and formation of micron-sized islands. Reduced substrate temperature or increased oxygen flux helped enhancing the nucleation to obtain continuous films by fast coalescence of densely packed nuclei [5]. Depending on application, suppressed wetting can be used to produce oxide islands, faceting can help defining the surface properties (e.g. for chemical sensors), and enhanced nucleation and prevented faceting helps to obtain smooth, continuous films that are required for most technological applications.

Systematic doping was studied for SnO$_2$ by the donor Sb [6] and the (deep)acceptors In [7] and Ga [8], and for In$_2$O$_3$ by the donor Sn [9] and the (deep)acceptor Mg [10]. Doping limits were identified by the formation of secondary crystalline phases [1, 9, 10], and Sn-incorporation into In$_2$O$_3$ was inhibited at high Sn-concentrations --- likely due to the preferential formation of parasitic Sn-suboxides [9]. High Sn-doping prevented the \{111\} faceting and enhanced the nucleation on YSZ [9].

3.2 Electron transport in SnO$_2$ and In$_2$O$_3$

Similar to most $n$-type transparent semiconducting oxides, SnO$_2$ and In$_2$O$_3$ are $n$-type conductive even in the absence of intentional donors --- they are unintentionally doped (UID). Our UID SnO$_2$ [6] and In$_2$O$_3$ [11] films showed electron concentrations due to shallow donors on the order of $10^{20}$cm$^{-3}$ at electron mobilities of ~100 and ~200 cm$^2$/Vs, respectively.

A surface electron accumulation layer was present in both oxides [13,14], which enhanced the formation of ohmic contacts [12] but prevented the formation of Schottky contacts [12—15]. A surface oxygen plasma treatment was able to deplete the accumulation [13, 14] and enable formation of Schottky contacts [12, 15]. Unlike in e.g. InN, the conductance contribution to the UID conductivity was negligible in both oxides [8, 14].

The resistivity of both oxides could be varied by doping over nine orders of magnitude from the highly conductive to the semi-insulating regime (Fig.2). Systematic Sb-doping of SnO$_2$ was performed for concentrations from $10^{16}$ to $2.6\times10^{20}$cm$^{-3}$ with high doping efficiency achieving a TCO-like conductivity [6] whereas acceptor doping with In and Ga allowed to make the SnO$_2$ semi-insulating [7,8] but not $p$-type conductive. At acceptor concentrations in excess of ~$10^{20}$cm$^{-3}$ the SnO$_2$ $n$-type conductivity of SnO$_2$ increased again.

Systematic donor doping of In$_2$O$_3$ with Sn allowed to achieve electron concentrations of $>10^{23}$cm$^{-3}$ and a resistivity of $10^4$ Ohm cm [9]. Doping by Mg allowed to achieve semi-insulating In$_2$O$_3$ but no $p$-type conductivity. The conductivity of In$_2$O$_3$ was strongly dependent on annealings in oxygen or vacuum, indicating that the native point defects oxygen vacancies and oxygen interstitials to play a major role as UID or compensating donors and compensating acceptors, respectively. The Seebeck coefficient and mobility of In$_2$O$_3$ as a function of electron concentration was measured and modeled [16]. Combined Hall and Seebeck measurements were able to prove the bulk character of our UID donors as opposed to surface donors.

![Fig. 2 Control of In$_2$O$_3$ resistivity by donor (Sn) and acceptor (Mg) doping.](image)

**References**


