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ABSTRACT

Significant resistivity variations have previously been observed in oxides subjected to relatively low ion irradiation doses, nominally insufficient to generate the amount of bulk defects needed to explain the phenomena. In an effort to unveil the underlying mechanisms, we performed a systematic comparative study of the resistivity evolution in In_2O_3-based oxides as a function of low ion doses and ultraviolet (UV) illumination, observing striking correlations. Specifically, we found that irradiation with $\sim 3 \times 10^{12}$ Si/cm^2 and ~18 h UV exposure result in similar resistivity drops, interpreted in terms of irradiation/illumination assisted desorption of oxygen containing species from the surface. This was further proven by post-irradiation exposure of one of the samples to an oxygen atmosphere partially restoring the resistivity. Combining the present results with literature data, we conclude that the radiation tolerance of In_2O_3-based and similar oxides depends on the surface charge modifications, individual defect contributions, and contributions from defect complexes at low, intermediate, and high doses, respectively.

I. INTRODUCTION

An intriguing property of certain wide bandgap semiconductors, such as InAs, InN, In_2O_3, SnO_2, and ZnO, is the accumulation of electrons at the surface,[1–4] in the form of a so-called surface electron accumulation layer (SEAL). While the surface of most other semiconductor materials tends to be electron deficient with respect to the bulk,[5] the SEAL results from a downward bending of the conduction band edge toward the surface. In ZnO, adsorbed hydrogen,[6] oxygen,[7,8] and OH groups[6] have all been found to correlate with a downward band bending, and for this specific material, the surface polarization also comes into play.[6] For In_2O_3, theoretical calculations have shown that an oxygen vacancy situated at the surface of the material may act as a shallow donor and could be the reason for the downward band bending.[9] In other words, there is currently no consensus of the source of the band bending, and the formation of the SEAL is not necessarily explained by one single model. However, it is clear that oxygen species adsorbing to the surface, e.g., from exposure to oxygen gas, ozone, or oxygen plasma, can

remove the downward band bending and even bend the conduction band upward, effectively removing the SEAL.[10–12] Interestingly, this effect can be reversed by exposure to ultraviolet (UV) light[12,13] or thermal annealing in vacuum,[14] which restores the downward surface band bending through desorption of the adsorbed molecules. These processes form the working principle of conductometric gas sensors.[10,15] Acceptor doping has been shown to be beneficial in increasing the sensitivity of a gas sensor through reducing the bulk contribution to the conductivity.[10] However, at a given acceptor concentration, the Fermi level is shifted below the surface conduction band and effectively drains the surface of electrons, thereby removing the SEAL as a conduction channel.[10]

The downward band bending and the resulting SEAL for InAs, InN, In_2O_3, SnO_2, and ZnO, is often explained in terms of the unusually high bulk material charge neutrality level (CNL) in these materials.[5] In two recent studies, we utilized ion irradiation to study the evolution of the electrical properties of several wide bandgap oxide semiconductors as a function of increasing defect concentration, i.e., irradiation dose.[16,17] Interestingly, we found that, e.g.,

in In_2O_3, where the CNL is commonly assumed to be positioned above the conduction band minimum (CBM),[18] the introduction of a low concentration of Frenkel pairs on both sub-lattices increases the acceptor concentration in the material. This was interpreted in terms of the charge state imbalance of the In vacancy and In interstitial. It was found that the effective acceptor doping increases the resistance of the material by more than an order of magnitude. However, as the irradiation dose is increased the formation probability of defect complexes also increases. Specifically, the formation of indium- and oxygen antisites[19] changes the charge balance, resulting in the recovery of the highly conducting n-type material.

In general, it was found that the resistance increase observed at doses between 10^{13} and 5×10^{14} cm^{-2}, and the subsequent decrease at doses exceeding ~10^{15} cm^{-2} is controlled by the positions of the charge transition levels for the intrinsic primary defects and intrinsic defect complexes, respectively. Interestingly, when irradiating ZnO, SnO_2, In_2O_3, In_2O_3:Sn, or $(InGa)_2O_3$:Mg with ion doses <10^{13} cm^{-2}, an initial reduction of the resistance is observed. This reduction cannot be explained in terms of defect interaction in the bulk of the material because (i) the introduced defect concentration is much lower than the background doping and (ii) the introduced Frenkel pairs are net acceptors, which would lead to an increase, rather than a decrease, of the resistance.

In this work, we have studied the resistivity evolution in In_2O_3 when irradiated with low ion doses. We propose that the ion irradiation, similar to UV illumination, interacts with the surface and leads to the formation of a surface electron accumulation layer (SEAL). The SEAL acts as an additional conduction channel, resulting in a reduced resistance.

II. EXPERIMENTS

$(In_{1-x}Ga_x)_2O_3$:Mg with $x = 17\%$ and 1% Mg doping was deposited on a single 10×10 mm^2 electrically insulating c-plane sapphire substrate using pulsed laser deposition (PLD). This composition was selected as it has a high, but still measurable, resistivity in the as-grown state. After growth, the sample was laser cut into two nominally identical 5×10 mm^2 samples labeled A and C, having resistances of 5.72×10^8 and 6.22×10^8 Ω, respectively. The relatively small difference in resistance was attributed to minor variations in the sample dimensions and the sizes and positions of the contacts. In addition, an In_2O_3:Mg sample with 0.5% Mg doping was deposited by PLD in the same chamber on a nominally identical substrate and is labeled sample B.

Contacts were formed by soldering silver wires to each end of the samples using indium as solder metal, and Ohmic behavior was confirmed through current–voltage measurements from −1 to 1 V.

The subsequent experiments were carried out at a pressure on the order of 10^{-6} Torr in a vacuum chamber connected to an NEC tandem ion implanter. As the three samples would undergo different experiments, only a single sample was present in the chamber at any given time.

Before ion irradiation, samples A and B were exposed to 250 nm ultraviolet (UV) illumination for ~18 h in order to remove adsorbed atoms and molecules from the surface. Sample C acted as a reference sample and was held under the same vacuum conditions as samples A and B for a similar time, but was not exposed to the UV light. Each sample was then irradiated with 3 MeV Si^{2+} ions in several stages,

and between each irradiation exposure, the resistance was measured *in situ* on a Keithley 6487 voltage source/picoammeter.

Following the irradiation of sample B to an accumulated dose of 5×10^{13} cm^{-2}, the surface was re-populated with adsorbates by exposure to 99.999% pure O_2 gas while monitoring its resistance.

III. RESULTS AND DISCUSSION

Figure 1 shows the resistance of samples A and B as function of time during 250 nm UV light illumination in high vacuum. Following an initial rapid decrease, the resistance of sample A is approaching a stable value of ~3.4×10^4 Ω. Relative to the initial value, this corresponds to a decrease of nearly four orders of magnitude over the course of the exposure, and is attributed to the removal of adsorbed atoms from the surface. These data are consistent with a downward surface band bending, as illustrated in Fig. 2, resulting in the formation of a SEAL through the release of electrons to the conduction band at, or close to, the surface. Sample B shows qualitatively similar behavior as sample A. Keeping sample C under the same conditions as samples A and B, but without the UV light exposure, causes its resistance to drop by a factor 2. That is, the vacuum has a far weaker effect on the resistance than the UV illumination that, following the above reasoning, shows that the UV light strongly promotes the desorption of surface adsorbates.

The resistance evolutions of samples A, B, and C as functions of irradiation dose are plotted in Fig. 3. Interestingly, for the illuminated samples (A and B), the ion irradiation has only a weak influence on the resistance in the measured dose range. Sample C, on the other hand, shows a dramatically different response to the ion irradiation. Irradiating this sample rapidly decreases its resistance, already from the first exposure. At a dose of ~3×10^{12} cm^{-2}, the resistance has dropped by 4 orders of magnitude from its as-grown value, consistent with In_2O_3 and ZnO samples reported in previous publications.[16,17] At these low doses, the bulk defect concentration introduced by the irradiation is too low to explain such a dramatic
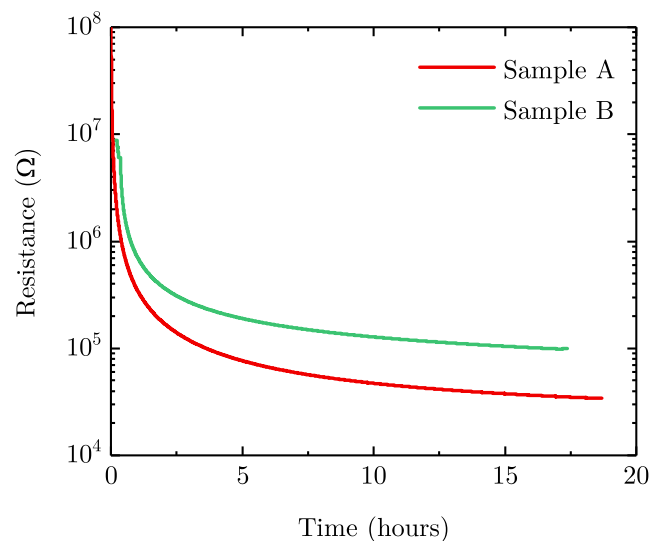

FIG. 1. The resistance evolution of samples A and B during 250 nm UV illumination.
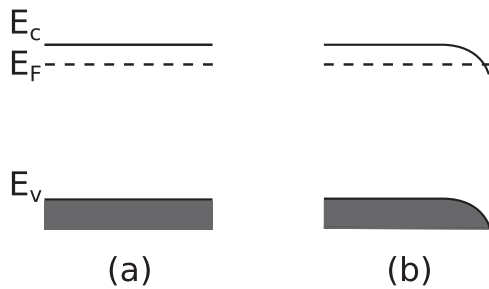
FIG. 2. Simplified illustration of the bulk and surface contributions to the band structure. (a) Flat band situation with surface saturated with adsorbates. (b) Removal of adsorbates by either UV-illumination or ion irradiation results in downward band bending at the surface.

resistivity drop. In Ref. 17, a concentration of 3.5×10^{17} cm^{-3} electrically active Frenkel pairs was estimated to have formed in In$_2$O$_3$ at a dose of 10^{12} cm^{-2}, i.e., more than one order of magnitude lower than the observed change in carrier concentration at this dose. Moreover, density functional theory (DFT)[19] proposes that the net charge state of Frenkel pairs forming in In$_2$O$_3$ at these Fermi levels is negative, i.e., the net generated defect population acts as acceptors, apparently contradicting the observed decrease in resistance. To reconcile the formation of bulk acceptor defects with the observed decrease in resistance, we look to the sample surface and its electron accumulation layer.[2] Comparing samples A and C, the similar response to overnight UV illumination and 3 MeV Si^{2+} irradiation may indicate that the effect originates from a common mechanism. In particular, removal of surface adsorbates is well established as the cause of the resistance decrease under UV illumination in the literature (see, e.g., Refs. 7 and 8 and references therein). Thus, we propose that a similar mechanism occurs also during ion irradiation.
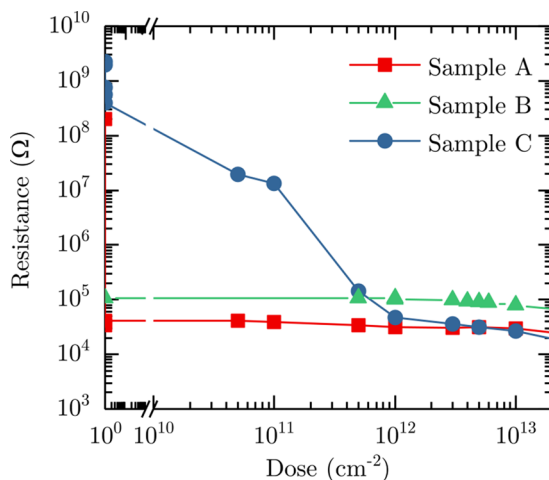
To further investigate the effect of surface adsorbates on the electrical properties of ion irradiated samples, the resistance of sample B was measured as a function of time during exposure to O$_2$ gas after ion irradiation to a dose of 5×10^{13} cm^{-2}. As shown in Fig. 4, the resistance initially increases rapidly when the gas is introduced, followed by a saturation stage. After 10 h the resistance has increased by a factor 5, and asymptotically approaches a stable value. This value is, however, still about a factor 30 lower than the original resistance of this sample, indicating either (a) that pure oxygen adsorbates are weaker electron traps than the species present on the surface during the original measurement or (b) that the ion irradiation has generated bulk donors. For pure indium oxide, the latter interpretation would be in conflict with our findings reported in Refs. 16 and 17, where the defects generated at a dose of 5×10^{13} cm^{-2} were found to be acceptors. However, the low Fermi level induced by the Mg doping of sample B could possibly make donor formation favorable already at this low dose.

The presented results show that the resistivity of In$_2$O$_3$ can be decreased both by UV illumination and ion irradiation, and subsequently increased by exposure to oxygen gas. Thus, we extend the model of defect concentration dependent resistivity presented in Refs. 16 and 17 by proposing that the resistivity reduction observed at ion doses $<10^{13}$ Si/cm^2 results from an irradiation induced downward surface band bending. Starting from a state where the surface is saturated with adsorbates and the valence-, conduction-, and Fermi levels are all flat, as illustrated schematically in Fig. 2(a), the downward band bending caused by removal of adsorbates is shown in Fig. 2(b).

With the addition of this analysis, our model for the defect concentration dependent resistance in oxides then contains three separate contributions: (i) an initial resistance decrease caused by surface modifications at low doses, (ii) a subsequent increase in
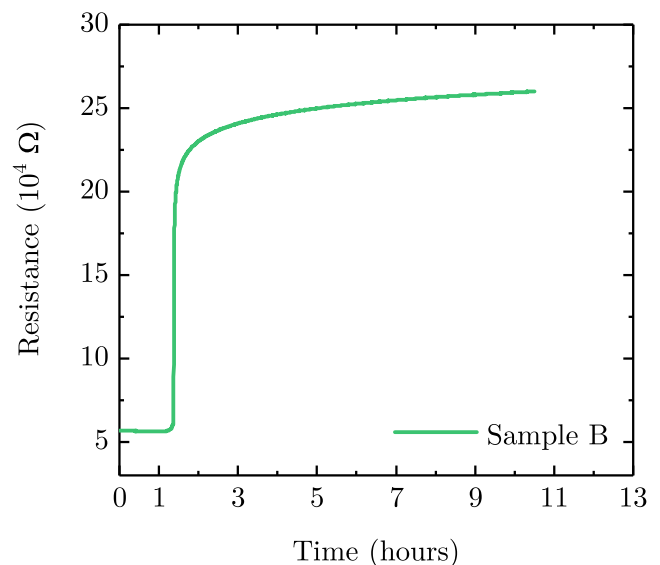

FIG. 3. Resistance of each sample as function of irradiation dose.

FIG. 4. Resistance of sample B during exposure to O$_2$ gas after irradiation. As the gas is introduced to the chamber between the 1 and 2 h marks the resistance initially increases sharply, before approaching a stable value.

resistance caused by individual point defects at intermediate doses, and (iii) a second resistance decrease due to the formation of defect complexes at high doses.

IV. CONCLUSIONS

Comparing the defect concentration dependent resistivity of In_2O_3 samples irradiated with and without prior UV illumination, the response to low dose irradiation is found to correlate with modifications of the surface properties of the samples. Specifically, the reduction in resistance at doses $\leq 10^{13}$ cm^{-2}, observed also in SnO_2 and ZnO,[16] can be explained by a downward band bending at the surface, enabling the establishment of a surface electron accumulation layer exhibiting a higher conductivity compared to that in the bulk.

The surface electron accumulation layer (SEAL) can be depleted by exposing the sample to O_2 gas, suggesting that adsorbed atoms or molecules flatten the bands and trap the delocalized conduction electrons.

The presented results complements the data on defect dependent resistivity collected in Refs. 16 and 17. The corresponding model then comprises three components, each with the possibility of affecting the resistivity, (i) modification of surface states at doses $\leq 10^{13}$ cm^{-2}, (ii) generation of individual bulk point defects at doses $\leq 10^{14}$ cm^{-2}, and (iii) agglomeration of point defects into complexes at higher doses. Depending on the net charge state of the defect population, each stage can increase or decrease the sample resistivity.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Jon Borgersen: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Validation (equal); Visualization (equal); Writing – original draft (lead); Writing – review & editing (equal). **Robert Karsthof**: Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Validation (equal); Writing – review & editing (equal). **Vegard Rønning**: Data curation (equal); Investigation (equal); Methodology (equal); Writing – review & editing (equal). **Lasse Vines**: Conceptualization (equal); Formal analysis (equal); Supervision (equal); Validation (equal); Writing – review & editing (equal). **Holger von Wenckstern**: Conceptualization (equal); Writing – review & editing (equal). **Marius Grundmann**: Funding acquisition (equal); Writing – review & editing (equal). **Andrej Yu. Kuznetsov**: Conceptualization (equal); Formal analysis (equal); Project administration (equal); Supervision (equal); Writing – review & editing (equal). **Klaus Magnus Johansen**: Conceptualization (equal); Data curation (equal); Project administration (equal); Supervision (equal); Visualization (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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