

THE CONDITIONS FOR DOPANT ACTIVATION IN TIN-DOPED GALLIUM OXIDE

Worldwide searches for new energy sources and innovative technologies to enable efficient energy generation and use are leading researchers to take second looks at many materials that evaded widespread commercialization in the past. One of these is gallium oxide (Ga_2O_3), which may prove valuable in optoelectronic devices that rely on a transparent conducting oxide to transport charge carriers and photons to and from active semiconductor layers. Tin (Sn)-doped beta-phase gallium oxide ($\beta\text{-Ga}_2\text{O}_3\text{:Sn}$) is one such promising candidate. To be used as thin films in commercial semiconductor devices, however, $\text{Ga}_2\text{O}_3\text{:Sn}$ would need to be deposited at lower temperatures. That presents a problem because laying down thin films of it using atomic-layer deposition (ALD) and pulsed-laser deposition (PLD) at moderate temperatures have not produced films with high Sn dopant activation. To find out why, scientists carried out studies at the APS that open a path to solving the problem while highlighting the important role that state-of-the-art synchrotron x-ray spectroscopic techniques can play in optimizing the growth of new materials that have the potential for widespread applications crucial for energy sustainability.

atomic arrangements and chemical states, and was used in this case to define the requirements for successful Sn dopant activation. While XAS studies focusing on Ga could be conducted at the Stanford Synchrotron Radiation Lightsource at the SLAC National Accelerator Laboratory, these researchers needed to study Sn *K*-edge spectra at the MR-CAT beamline 10-ID-B of the APS because its brilliant, high-energy x-rays were required to probe the much heavier element.

The chemical states of Sn for the crystalline and amorphous samples were revealed by comparing the respective *K*-edge x-ray absorption near-edge structures (XANES) with XANES data from Sn metal foil, SnO powder, and SnO₂ powder reference samples, because the chemical shifts observed in the XANES spectra were due to changes in the oxidation state of the Sn atoms (Fig. 1). The researchers found that the average charge state of the active Sn dopant atoms in $\beta\text{-Ga}_2\text{O}_3\text{:Sn}$ was similar to that of SnO₂ (+4 charge state). By contrast, the Sn dopant atoms in resistive $\text{Ga}_2\text{O}_3\text{:Sn}$ samples grown by PLD and ALD were present in either +2 or +4 charge states, depending on growth conditions. In both cases, the Sn dopant atoms were inactive.

Next, extended x-ray absorption fine structure (EXAFS) spectroscopy was used to investigate details of the Sn doping in each form of $\text{Ga}_2\text{O}_3\text{:Sn}$. The Ga in un-doped Ga_2O_3 coordinates with oxygen atoms both tetrahedrally and octahedrally. In $\beta\text{-Ga}_2\text{O}_3\text{:Sn}$, the activated Sn dopant atoms preferentially substituted for the octahedrally coordinated Ga atoms, which was not the case in a $\text{Ga}_2\text{O}_3\text{:Sn}$. Furthermore, the EXAFS results showed structural order beyond the first nearest neighbor shell of atoms in $\beta\text{-Ga}_2\text{O}_3\text{:Sn}$, but a lack of such ordering in the amorphous $\text{Ga}_2\text{O}_3\text{:Sn}$ samples (Fig. 2), which indicates that a crystalline structure may be necessary for high dopant activation.

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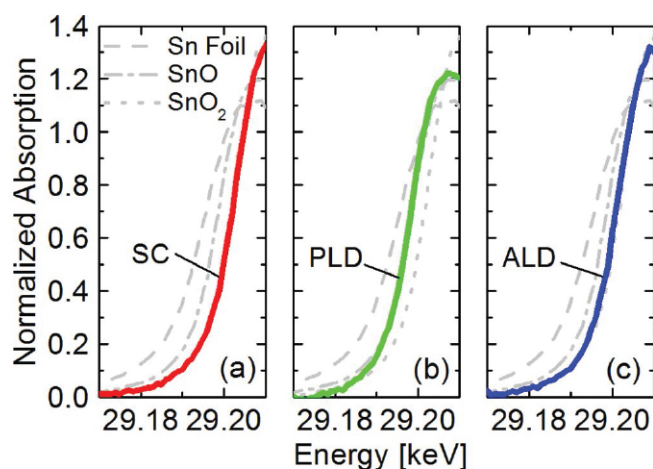


Fig. 1. Sn *K*-edge XANES spectra for (a) single crystal (SC) $\beta\text{-Ga}_2\text{O}_3\text{:Sn}$, (b) PLD $\alpha\text{-Ga}_2\text{O}_3\text{:Sn}$, and (c) ALD $\alpha\text{-Ga}_2\text{O}_3\text{:Sn}$ samples. The dashed, dashed-dotted, and dotted lines represent the Sn(0) metal (dashed line), Sn(+2)O (dashed-dotted line), and Sn(+4)O₂ (dotted line) reference samples, respectively.

Tin (Sn)-doped beta-phase gallium oxide ($\beta\text{-Ga}_2\text{O}_3\text{:Sn}$) has a wide bandgap, low electron affinity, a high electron donor concentration, and transmissivity to light above 80% in the 300–1000 wavelength range. $\beta\text{-Ga}_2\text{O}_3\text{:Sn}$ having high donor concentration can be produced by growing bulk

single crystals at 1725° C and by depositing the material via molecular beam epitaxy at temperatures in the 540-600° C range. The researchers from the Massachusetts Institute of Technology, Harvard University, the Illinois Institute of Technology, Stanford University, the SLAC National

Accelerator Laboratory, Helmholtz-Zentrum Berlin (Germany), and the National Renewable Energy Laboratory compared $\beta\text{-Ga}_2\text{O}_3\text{:Sn}$ bulk single crystals to amorphous $\text{Ga}_2\text{O}_3\text{:Sn}$ ($\alpha\text{-Ga}_2\text{O}_3\text{:Sn}$) thin films deposited by ALD and PLD at temperatures <300° C, using two versions of *K*-edge x-ray absorption spectroscopy (XAS), which probes for local

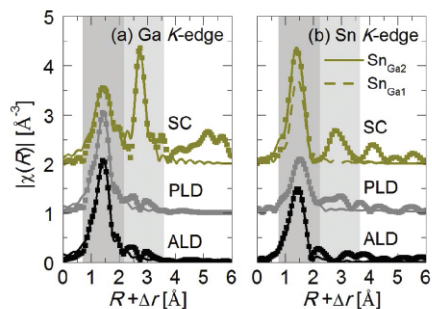


Fig. 2. EXAFS spectra for (a) Ga and (b) Sn K-edges. The dark and light grey regions represent the first and second nearest-neighbor shells for the single crystal sample at the Sn K-edge. Note the good fit for Sn on the Ga_2 octahedral site for the single crystal (SC) sample and the lack of structural order beyond the first nearest-neighbor shell for the ALD and PLD samples.

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These observations suggest the importance of growing $\text{Ga}_2\text{O}_3:\text{Sn}$ at high temperature to obtain a crystalline phase and the need to control the oxidation state of Sn during growth to achieve dopant activation.

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10-ID-B • MR-CAT • Materials science, environmental science, chemistry • X-ray absorption fine structure, time-resolved x-ray absorption fine structure, micro x-ray absorption fine structure, microfluorescence (hard x-ray) • 4.3-27 keV, 4.3-32 keV, 15-90 keV • On-site • Accepting general users •