Relating oxygen vacancies to $\beta - Ga_2O_3$ unintentional n-type doping

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Reading from *"Recent progress on the electronic structure, defect, and doping properties of Ga_2O_3"* by Jiaye Zhang and others, they have a section on unintentional n-type doping in $\beta - Ga_2O_3$. They then describe how there is no consensus on why this occurs, but give some merit to oxygen vacancies (V_o).

0.1 Oxygen Vacancies

Oxygen vacancies in metal-oxide semiconductors would occur during the crystal-growth process. In Floating Zone (FZ) growth, the growth environment would have some level of oxygen that can be controlled. Experimental data in the paper plotted the grown $\beta - Ga_2O_3$ crsytal's oconductivity to be inversely proportional to the oxygen flow rate in the growth environment, which could be related to the partial pressure of oxygen in the growth environment (P_{O_2}).

$$\sigma \propto \frac{1}{P_{O_2}} \tag{1}$$

So the question is, why does this cause, or how can we show mathematically why oxygen vacancies (V_o) cause n-type conductivity.

But, it can be explained with the Fermi Level E_F.

0.2 The Fermi Level

In the textbook, we can describe the distance between the Fermi Level and the energy in the conduction band with this equation:

$$E_c - E_F = kT \ln \frac{N_c}{n_0} \tag{2}$$

Where we know that as the Fermi Level approaches the conduction band, as in $E_c - E_F \to 0$, the material becomes n-type conductive.

Assuming that temperature is stable, we can see what happens to the effective density of states function in the conduction band N_c. This parameter describing what energy states the electrons (our material's majority carrier) have to work with within the conduction band.

0.2.1 Connecting N_c to V_o

Empirically, we see larger conductivities for lower oxygen rates, or more oxygen vacancies.

$$\uparrow V_o \implies \uparrow \sigma \tag{3}$$

Then we know that increases in electric conductivity is directly proportional to electron mobility.

$$\sigma \propto \mu_n \tag{4}$$

Electron mobility is given by this equation in the textbook:

$$\mu_n = \frac{q\tau}{m_n^*} \tag{5}$$

And given this equation for the effective density of states function in the conduction band from the textbook:

$$N_c = 2\left(\frac{2\pi m_n^* kT}{h^2}\right)^{3/2} \tag{6}$$

Which shows $N_c \propto (m_n^*)^{3/2}$. So now we can make this connection.

$$\uparrow V_o \implies \uparrow \sigma \implies \uparrow \mu_n \implies \downarrow m_n^* \implies \downarrow N_c \tag{7}$$

Or:

$$V_o \propto 1/N_c \tag{8}$$

0.2.2 Evaluating $N_c \to n_0$

From experimental data $N_c \sim 10^{19}$ and $n_0 \sim 10^{17}$ for $\beta - Ga_2O_3$; if not, $N_c > n_0$, generally.

If we assume this we can perform a limit on the distance between the conduction band and the Fermi level as $N_c \to n_0$, which mimics the relationship of V_o and N_c.

$$\lim_{N_c \to n_0} (E_c - E_F) = \lim_{N_c \to n_0} \left(kT \ln \frac{N_c}{n_0}\right) = kT \ln 1 = 0 \tag{9}$$

So, the oxygen vanancies V_o cause the Fermi Level E_F to approach the conduction band energy E_c, which is the property of a n-type material.