Growth of Zn-Ge-O Thin Film as a Transparent Conductive Oxide With a Low Electron Affinity

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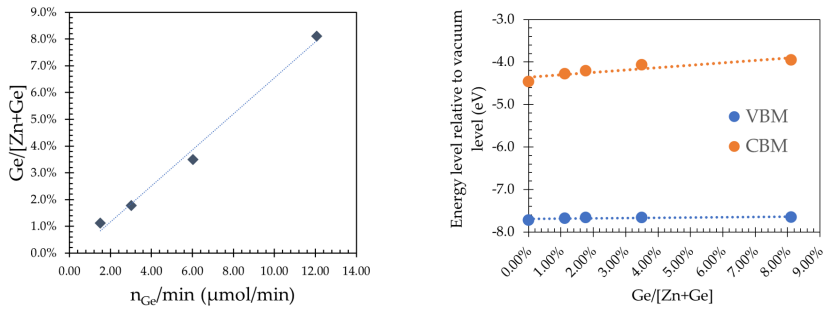
Transparent conductive oxides (TCOs) have been widely used in optical and electrical device applications such as solar cells, ultraviolet lasers, sensors, light-emitting diodes, and transparent electrodes owing to their high optical transparency and electrical conductivity. Among the TCOs, zinc oxide (ZnO) has been very attractive for transparent contact applications such as in Cu(In,Ga)(S,Se)$_2$ (CIG(SSe)$_2$) solar cell due to the low material cost, low growth temperature, and non-toxicity. The band gap of i-ZnO has been estimated to be around 3.3 eV, with the conduction band energy level located around −4.4 eV under the vacuum level. This material property is suitable for the narrow band gap CIG(SSe)$_2$. However, considering the diversity of CIG(SSe)$_2$ material, the use of i-ZnO as the front contact of the wider band gap CIG(SSe)$_2$ might not yield the same result due to the mismatch of the conduction band alignment. Previous studies have attempted mixture of metals such as Mg to alter the band gap characteristics of the ZnO film and improve the conduction band alignment. However, the metal oxides of these materials tend to have very large band gaps, thus increasing the difficulty of precise band control. Another metal that has the potential to be combined with ZnO is Ge. In addition, the band gap of GeO_2 at 3.9-5.9 eV is relatively closer to ZnO. In this study, we propose a new n-type material formed by Zn-Ge-O elements as an alternative transparent conductive oxide material with a low electron affinity.

Zn-Ge-O film was deposited on a soda lime glass (SLG) substrate in a Metal-Oxide Chemical Vapour Deposition (MOCVD) system with the substrate temperature at 158 °C under 3.0 Torr chamber pressure. The Zn, Ge, and O material sources are $(C_2H_5)_2Zn$ or DEZ, $Ge(OCH_3)_4$, and H_2O respectively. The materials are deposited through Ar carrier gas and the concentrations are controlled through the flow rate. All deposited samples are non-doped, and a reference ZnO was also deposited through the MOCVD method under the same growth condition. The films were characterised through some measurements such as ICP-AES, UV-Vis spectra, and ionisation energy.

We determined the Ge and Zn concentration in the film through ICP-AES measurement. As shown in Figure 1a, we have succeeded in controlling the Ge-content through the material flow rate, with the flow rate to content ratio around 2.2-2.8 times. The ionisation energy and UV-Vis spectra measurements confirmed that an increase of Ge-content resulted in widening of the band gap, which was mainly the result of changes in the conduction band as illustrated in Figure 1b. Thus, we have demonstrated the potential of conduction band alignment control for wide band gap CIG(SSe)$_2$ front contact application in the MOCVD grown Zn-Ge-O thin film TCO.



(a) (b)

Figure 1: (a) Ge-source flow rate and (b) energy levels of the Zn-Ge-O films in relation to the Ge/[Zn+Ge] ratio.

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