Excitonic blue luminescence from p-LaCuOSe/n-InGaZn5O8 light-emitting diode at room temperature
Excitonic blue luminescence from $p$-LaCuOSe/$n$-InGaZn$_5$O$_8$ light-emitting diode at room temperature

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A hetero $p/n$ junction diode was fabricated by laminating an amorphous $n$-type InGaZn$_5$O$_8$ layer to a $p$-type LaCuOSe film epitaxially grown on a MgO (001) substrate. It exhibited a relatively sharp blue electroluminescence (EL) that peaked at ~430 nm at room temperature when a forward bias voltage above 8 V was applied. The wavelength and bandwidth of the EL band agreed well with those of the excitonic photoluminescence band in LaCuOSe, which indicates that the EL band originates from the exciton in LaCuOSe. This experiment strongly suggests that layered compounds, LaCuOCh ($Ln=$lanthanide, $Ch=$chalcogen), are promising as the light-emitting layer in optoelectronic devices that operate in the blue–ultraviolet region. © 2005 American Institute of Physics. [DOI: 10.1063/1.2133907]

Wide bandgap semiconductors such as diamond, GaN, ZnSe, and ZnO have attracted much attention for their applications in optoelectronic devices that operate in the short-wavelength region. Layered oxchalcogenides, LaCuOCh ($Ln=$lanthanide, $Ch=$chalcogen), whose structures are composed of alternating stacks of (La$_2$O$_2$)$_{2+}$ and (Cu$_2$Ch)$_{2-}$ layers along the $c$-axis, are wide gap $p$-type semiconductors. These semiconductors have several distinct features favorable for optoelectronic devices such as wide bandgaps between ~2.8–3.1 eV that are tunable by substituting $Ch$ ions, large exciton binding energies of ~50 meV, and $p$-type conduction with a large Hall mobility (8 cm$^2$ V$^{-1}$ s$^{-1}$) for undoped LaCuOSe. These features mostly originate from their two-dimensional crystal and electronic structures, which are analogous to semiconductor artificial superlattices such as the GaAs/AlGaAs multiple quantum well (MQW). For example, the binding energy of the exciton is significantly enhanced due to the confinement of the hole carriers to the (Cu$_2$Ch)$_{2-}$ layers, and the bandgaps are widened presumably due to the two-dimensional structure. Another noticeable achievement that has resulted from the quasi-MQW structure is the realization of degenerate $p$-type conduction in Mg-doped LaCuOSe. This success is primarily attributed to the delta doping mechanism, i.e., high-density substitution of La$^{3+}$ sites with Mg$^{2+}$ ions is achieved in the (La$_2$O$_2$)$_{2+}$ layer and the generated holes are transferred to the (Cu$_2$Se)$_{2-}$ layer (the hole carrier path) due to the large local band offset at the valence band maximum between the (La$_2$O$_2$)$_{2+}$ and (Cu$_2$Se)$_{2-}$ layers. The resultant spatial separation between the holes and the ionized acceptors allows the hole mobility to remain relatively large (~4.0 cm$^2$ V$^{-1}$ s$^{-1}$), even at a high carrier density (~10$^{20}$ cm$^{-3}$). Furthermore, it is noteworthy that the exciton in LaCuOSe is also stable at room temperature, despite the high hole density. That is, the exhibition of efficient blue–ultraviolet photoluminescence (PL) associated with the room temperature exciton and the formation of good $p$-type conductors make LaCuOCh promising materials for optoelectronic devices that operate in the short-wavelength region. One drawback of these semiconductors is that $n$-type conductors are difficult to form, making it impossible to fabricate a homo $p/n$ junction.

In this letter, we demonstrate the fabrication of a hetero $p/n$ junction by depositing an $n$-type amorphous indium gallium zinc oxide [a-InGaZn$_5$O$_8$ (a-IGZO), the band gap is ~3.5 eV] layer on a $p$-type epitaxial LaCuOSe film. When the applied forward bias voltage exceeds 8 V, the hetero $p/n$ junction exhibits a blue emission centered at ~430 nm, which is due to the recombination of the intrinsic exciton in the LaCuOSe layer.

Figure 1 illustrates the device structure of a light-emitting diode (LED) composed of the hetero $p/n$ junction. The LaCuOSe layer (thickness: ~350 nm) was initially grown on a MgO (001) substrate by a reactive solid-phase epitaxy (R-SPE) technique using a metallic Cu sacrificial layer (~5 nm thick). High-resolution x-ray diffraction measurements confirmed that the LaCuOSe layer was epitaxially grown on the MgO (001). Hall measurement using the van der Pauw configuration revealed that the film had a hole concentration of $1 \times 10^{19}$ cm$^{-3}$ and a mobility of 8 cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature. Subsequently, the $n$-type a-IGZO layer (~250 nm) was deposited by pulsed laser deposition (PLD) at room temperature using a ceramic target with a nominal composition of InGaZn$_5$O$_8$. The area of the $n$-layer was defined to a 800 μm diameter using a metal.

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The x-ray diffraction pattern of an a-IGZO film deposited on a glass substrate under the same deposition conditions showed only a halo, indicating that the film was in the amorphous phase. The concentration and mobility of the electron carrier at room temperature were \(1 \times 10^{19}\) cm\(^{-3}\) and 5 cm\(^2\) V\(^{-1}\) s\(^{-1}\), respectively. There are two reasons for this: one is that the low-temperature deposition prevents the LaCuOSe layer, which decomposes in a vacuum at high temperatures above \(\sim 400^\circ\)C, from degrading and enables it to be used as the light-emitting layer. The second reason is that the bandgap of a-IGZO is larger than that of LaCuOSe in order to induce the recombination of electrons and holes in the LaCuOSe layer. Finally, Au metal electrodes with a 500 \(\mu\)m diameter were deposited on both layers by sputtering through a metal mask.

Figure 2 shows the current-voltage characteristic of the \(p/n\) junction measured at room temperature, which exhibits a clear nonlinearity (non-Ohmic) and an asymmetric behavior with respect to the polarity of the applied voltage. Since the electric contacts of both the Au/a-IGZO and LaCuOSe/Au interfaces were experimentally confirmed to be Ohmic using a coplanar electrodes test pattern, the non-Ohmic behavior is attributed to the nature of the \(p/n\) junction. A slight leakage current, which increases with the forward bias voltage \(V_{\text{forward}}\), is observed below \(V_{\text{forward}} = 6\) V. Above that, the forward current \(I_{\text{forward}}\) abruptly increases. The threshold voltage \((\sim 6\) V\) is considerably larger than the bandgaps of LaCuOSe \((\sim 2.8\) eV\) and a-InGaZnO \((\sim 3.5\) eV\)). This may be due to the voltage drop from a series resistance caused by the bottom LaCuOSe layer since the electrons must flow long distances through the LaCuOSe layer to reach the junction area from the electrode.

A slight leakage current was also observed in the small reverse bias voltages \(V_{\text{reverse}}\) region probably due to the formation of a defective interface and the low temperature fabrication of the junction. In the large \(V_{\text{reverse}}\) region, a relatively large leakage current was detected. It is known that similar behavior is observed in a hetero \(p/n\) junction,\(^{18}\) where a reverse current \(I_{\text{reverse}}\) increases exponentially with \(V_{\text{reverse}}\) if a positive reverse barrier exists at the heterojunction. Although the current-voltage characteristic in Fig. 2 may reflect the intrinsic nature of the heterojunction, the possibility of the defective interface is not excluded as the origin of the large \(I_{\text{reverse}}\) in the large \(V_{\text{reverse}}\) region because the \(I_{\text{reverse}}\) does not follow the exponential behavior, and the non-negligible leakage current is also observed in the \(V_{\text{forward}}\) region. There also remains a possibility that the large \(I_{\text{reverse}}\) in the large \(V_{\text{reverse}}\) region is partly due to direct tunneling, such as observed in Esaki tunneling diodes\(^{19}\) since both the \(n\)- and \(p\)-layers have been highly doped at carrier densities of \(1 \times 10^{19}\) cm\(^{-3}\). Consequently, the rectifying ratio at the applied voltages of \(\pm 8\) V is as low as \(\sim 10^3\).

Figure 3 shows the EL spectra of the \(p/n\) junction measured at room temperature as a function of the injected current density. The EL spectra were monitored from the bottom of the MgO substrate by a fiber bundle attached to a spectrometer. A sharp blue EL band that peaked at \(\sim 430\) nm initially appears at \(V_{\text{forward}} = 8\) V (this corresponds to a current density of \(\sim 1.4\) A cm\(^{-2}\)), which is slightly larger than the threshold value of the current-voltage characteristic. The intensity increases with \(V_{\text{forward}}\) and tends to saturate with a further increase in \(V_{\text{forward}}\).

Figure 4 shows the PL and optical absorption spectra of a LaCuOSe epitaxial film compared to the EL spectrum of the \(p/n\) junction at \(I_{\text{forward}} = 2.5\) A cm\(^{-2}\). Two sharp peaks with an energy splitting of 125 meV are clearly observed in the absorption spectrum. The splitting is attributed to the excitons split by the spin-orbit interaction of a Se ion.\(^{8}\) A sharp emission peak is observed just below the lower-energy absorption peak at 2.9 eV in the PL spectrum, which is attributed to the recombination of the intrinsic exciton. The wavelength and bandwidth of the PL spectrum agree well
with those of the EL spectrum. That is, the electrons injected from the $p$-type IGZO layer are coupled with the preexisting holes in the $p$-type LaCuOSe layer to form excitons, which are annihilated by emitting blue luminescence. In addition to the excitonic emission, weak EL bands are observed at $\sim$480 and $\sim$600 nm, which are probably associated with in-gap states formed by Cu vacancy.

In summary, we demonstrated the room temperature operation of LED using a hetero $p/n$ junction composed of a wide bandgap $p$-type oxychalcogenide LaCuOSe, and an $n$-type amorphous InGaZnO$_4$. A blue EL band, which peaks at $\sim$430 nm and is associated with the intrinsic excitation of LaCuOSe, is observed at room temperature by applying a forward bias voltage above $\sim$8 V. The successful operation of the LED device at room temperature indicates that layered oxychalcogenides $LnCuOCh(Ln=$lanthanide, $Ch=$chalcogen) have a substantial potential as the light-emitting layer in optoelectronic devices that operate in the blue-ultraviolet region.