

Engineering of optically defect free Cu₂O enabling exciton luminescence at room temperature

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Abstract: Cu₂O is an interesting semiconductor with extraordinary high exciton binding energy, however exhibiting weak room temperature excitonic luminescence. The issue was addressed in literature emphasizing a detrimental role of native point defects responsible for optical quenching. Resolving the problem, we propose a method to manipulate the Cu and O vacancies contents opening a gateway for optoelectronic applications of Cu₂O. Specifically, applying oxygen lean conditions, we observe a remarkable suppression of V_{Cu} enabling strong room temperature exciton luminescence, while manipulating with V_O reveals no impact on the signal. As a result, the excitonic signature was interpreted in terms of phonon assisted transitions.

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OCIS codes: (250.5230) Photoluminescence; (130.5990) Semiconductors; (310.6860) Thin films, optical properties.

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21. The VO signature at ~750 nm, is still attributed to the doubly charged V_O, however slightly shifted to the longer wavelength as compared to that of 720 nm in [13], in part due to the band gap narrowing.
22. Using this logic it may be anticipated that the sample oxidized at 300°C might yield the strongest V_O signal, but due to its generally low crystallinity, the PL intensity is damped by non-radiative recombination channels.

1. Introduction

Cuprous oxide (Cu₂O) was extensively used during early-stage explorations in experimental semiconductor physics, while recently the interest to Cu₂O was reignited on behalf of possibilities to apply it in a number of key enabling technologies, including thin film transistors [1], resistive random access memories [2], photovoltaics [3], water splitting [4], spintronics [5], etc. Meanwhile, the initial role of Cu₂O – as a laboratory system to understand fundamental principles – was also renewed since excitons in Cu₂O were proposed as promising candidates for realization of Bose-Einstein condensation (BEC) at reasonably high temperatures [6, 7]. Indeed, the excitons in Cu₂O exhibit a unique combination of interesting properties, specifically, high binding energy, weak exciton-photon coupling, as well as a repulsive exciton-exciton potential [8]. However, in spite of extraordinary high exciton binding energy of ~150 meV, there is surprisingly limited data documenting room temperature exciton observations [9–12]. In one of the successful experiments, S. W. Snoke *et al* were able to detect phonon assisted yellow 1s exciton signatures at room temperature only using resonant excitation even utilizing high-purity single crystal Cu₂O [11]. The interpretation for this complexity was in terms of dominating direct band-to-band recombination without free carrier thermalization to the exciton ground state, while possible impurity/defect related quenching mechanisms were not taken into account. More recently, T. Ito *et al* carried out a dedicated photoluminescence (PL) study of Cu₂O synthesized in different conditions including natural bulk single crystals [12, 13]. The conclusion was that in all sorts of samples studied, defect-related luminescence dominates at least at >4.2K. Importantly, the exciton-related signal vanished already at ~260K [12] that was explained in terms of a bound state of exciton coupled – primarily – to copper vacancy (V_{Cu}), while oxygen vacancy (V_O) was assumed to be less significant recombination channel.

Thus, the effective exciton density/lifetime appears to be insufficient to explore optoelectronic potential of Cu₂O in full, in spite of nominally excellent combination of its properties. A possible solution of the problem would be to use "defect free" Cu₂O, specifically in terms of V_{Cu} and V_O, preventing optical quenching. There is a variety of methods reported for Cu₂O synthesis in literature: direct oxidation [3], floating zone [12], magnetron sputtering [14], metal organic chemical vapor deposition [15], etc. In most of the cases, the synthesis takes place at relatively high partial pressure of oxygen gas – in order to achieve reasonable growth rates – so that suppressing of both V_{Cu} and V_O is tricky. However, the dilemma may be resolved by applying more aggressive oxidants. In the present work, we applied low pressure oxygen plasma instead of oxygen gas maintaining reasonable growth rates and, concurrently affecting both V_{Cu} and V_O contents. As a result, we have observed exceptionally strong exciton transition dominating PL spectra at room temperature

suggesting that the present methodology may be readily used for further studies of exciton physics in semiconductors as well as exploration of optoelectronic applications.

2. Experimental

The samples were fabricated in a vacuum chamber (keeping the background pressure in the lower range of 10^{-7} Pa) commonly used for radio frequency plasma assisted molecular beam epitaxy (MBE) of oxide semiconductors employing oxygen radicals (5N5) as oxidants [16]. A conventional Knudsen cell was used to deliver metallic Cu (6N) while the oxide was formed in two different ways: (i) via post-oxidation of Cu films initially deposited on the substrates – referred as “oxidized” samples below or (ii) via standard MBE growth – referred as “epi” samples below. In either case, the oxygen pressure was maintained in the range of 10^{-3} Pa resulting in 100-150 nm thick Cu_2O films. The epi-samples were synthesized at 650°C [17], while the oxidized samples were processed in the range of $300\text{--}750^\circ\text{C}$. Some selected samples were subjected to post-fabrication anneals in oxygen gas (also at $\sim 10^{-3}$ Pa) at 750°C . The structural quality of the films was studied using x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS), while PL spectra were detected upon a 532 nm YAG laser excitation at room temperature. Two types of substrates were used in these experiments: c-plane Al_2O_3 – referred as “sapphire” below, and c-plane Al_2O_3 buffered with a 400 nm ZnO film – referred as “ZnO” below.

3. Results and discussion

Figure 1 shows XRD θ - 2θ scans taken from the epi and oxidized samples. Importantly, no signatures of either Cu or CuO phases are resolved in Fig. 1. Interestingly, the ex-situ XPS tests showed that the top surface layer of the films contains copper in its Cu^{2+} oxidation state, which however disappears already upon 5nm sputtering of the film (not shown but attributed to the long-term exposure to air). Importantly, the as-sputtered fresh surface showed no tracers of Cu^{2+} . Meanwhile, depending on the preparation method, there is a natural evolution in structural quality of the samples. For example, the high-temperature oxidized films on ZnO show an extra Cu_2O (200) peak at 42.3° , which is not seen in the epi samples and low-temperature oxidized sample. Overall, the phase homogeneity issues are critical but have been addressed/mastered earlier [18, 19], providing the grounds to focus on the evolution of the PL signatures as a function of oxidizing temperature.

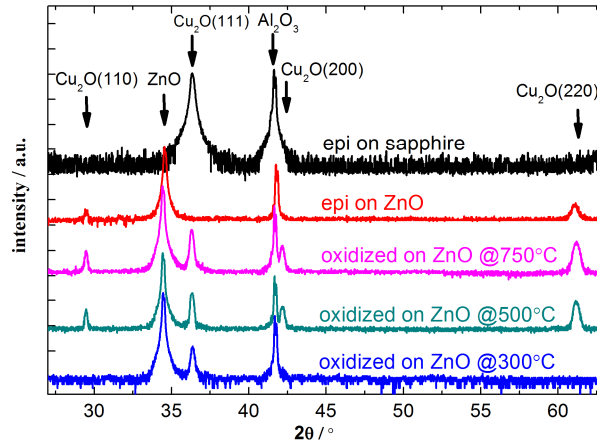


Fig. 1. XRD θ - 2θ scans of Cu_2O films.

Figure 2 shows PL spectra of the oxidized and post-fabrication annealed samples, while arrows indicate positions related to green 2p/yellow 1s excitons (G2/Y1), different charge states of V_O , and V_Cu as established in literature [10–13]. Spectacularly, exciton luminescence is clearly observed in all samples in Fig. 2, correlating with no signatures

associated with V_{Cu} . The last observation is extraordinary because, oxides with oxidizable cation generally tend to be cation-deficient in broad terms [20]. The apparent suppression of the V_{Cu} formation in our samples is a direct consequence of low oxygen pressure used in the present experiment comparing to the previous studies [3, 12–15]. Commonly, the oxygen pressure during Cu_2O synthesis ranges from 10^{-1} Pa range (e.g. in magnetron sputtering) to atmospheric pressure ($\sim 10^5$ Pa) for direct oxidation, meaning oxygen-rich growth conditions. Reducing oxygen gas pressure is no good alternative due to the growth rate limitations; however it apparently works well when using oxygen radicals, when lowering the pressure down to $\sim 10^{-3}$ Pa and shifting the balance toward oxygen lean conditions, evidently suppressing V_{Cu} , see Fig. 2.

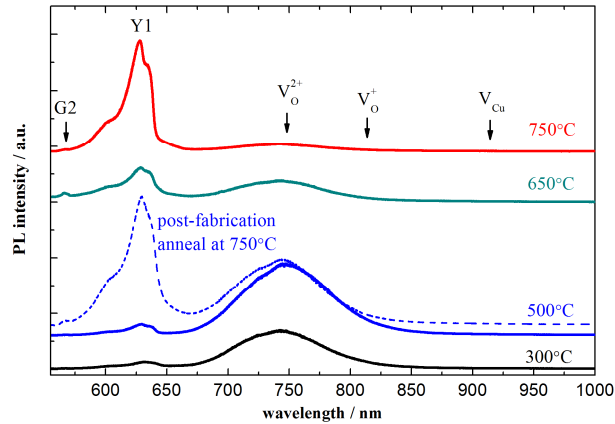


Fig. 2. Photoluminescence spectra of Cu_2O samples fabricated by direct oxidation of metallic Cu films on ZnO as a function of temperature. The dashed line represents the sample synthesized at $500^\circ C$ and subjected to a $750^\circ C$ post-fabrication anneal for 10 min.

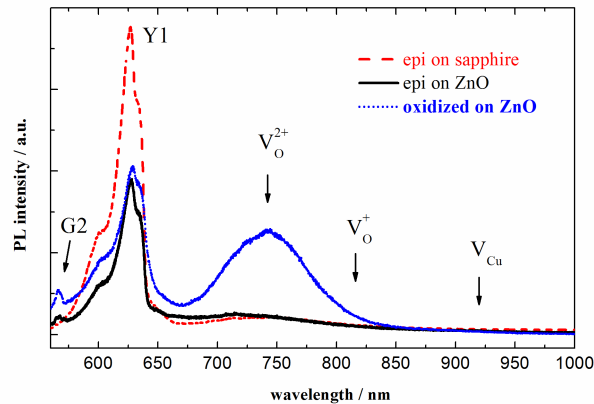


Fig. 3. Comparison of the photoluminescence spectra of oxidized and epi samples fabricated at $650^\circ C$ on ZnO, and epi sample fabricated at $700^\circ C$ on sapphire.

Notably, the Y1 signal rises with increasing the oxidizing temperature, reflecting the evolution/improvements in the crystal quality, see Fig. 1. The evolution with the G2 signature is less pronounced but follows a similar trend. Another interesting evolution occurs with the V_O signature [21]. Accounting that the PL peak magnitudes are proportional to the defect contents, there is a clear trend of decreasing V_O concentration in the samples oxidized at $\geq 650^\circ C$ [22] that could be potentially attributed to the temperature activated V_O mobility. However, the post-fabrication anneal (at $750^\circ C$) of the sample oxidized at $500^\circ C$ revealed no

impact on the V_O -related signature while the excitonic luminescence improved dramatically (see the dashed line in Fig. 2).

Thus, the exciton/defect PL signal ratios may be dramatically improved already in the course of a direct Cu oxidation, but the V_O -related signature remains even upon processing at high temperatures, which, by itself, is risky because of the fragile conditions for the Cu_2O single phase equilibrium. In this sense, gentle layer-by-layer oxidation in the course of the MBE growth using conditions selected from the direct oxidation experiments may provide more arguments for the interpretation.

In order to make a direct comparison, Fig. 3 shows PL spectra of the epi and oxidized samples on ZnO fabricated at 650°C, as well as the epi sample on sapphire at 700°C, applying identical oxygen plasma as oxidants. Notably, for the samples on ZnO, the exciton related peaks (both Y1 and G2) are nearly identical, while there is a dramatic difference in the V_O related luminescence – it is practically suppressed in the epi-sample. This implies that V_O , in contrast from V_{Cu} , may not be so critical for exciton studies in Cu_2O in accordance with an earlier hypothesis by Ito *et al.* [14]. It is worth to mention that, the epi sample on sapphire, demonstrate nearly identical line shape to the epi sample on ZnO except the higher intensity, which could be explained by the improved crystalline quality resulted from the higher synthesis temperature.

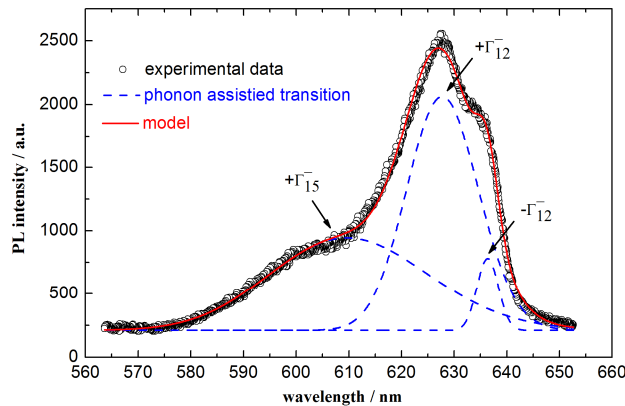


Fig. 4. Y1 excitonic signature as observed from the epi-sample on sapphire in Fig. 3 and modeled in terms of the allowed phonon assisted transitions.

At this end, the objective of the present communication is fulfilled – we demonstrated “optically” defect free Cu_2O enabling strong room temperature exciton luminescence and discriminated between the V_{Cu}/V_O roles to affect excitonic transitions. Altogether it might strengthen the interest to Cu_2O in terms of basic physics and applications calling for further dedicated studies. Meanwhile, Fig. 4 provides a preliminary analysis of the Y1 signature of the epi-sample in Fig. 3. The multiple peak character as clearly revealed in Fig. 4, and is because the direct dipole transition is forbidden due to the parity conservation resulting in the recombination assisted by phonons. In the first approximation, the shapes of such phonon-assisted components are determined by the kinetic energy distribution of excitons and the intensity related to the exciton-phonon coupling. In equilibrium, the excitons obeys Maxwell-Boltzmann distribution so that the components in Fig. 4, can be modeled by $I(E) \propto n(E) \propto (E - E_{ex} \pm E_p)^{1/2 - E/kT}$, where E , E_{ex} and E_p are the photon energy, the exciton binding energy, and the phonon energy, respectively, while k is Boltzmann constant, T is the temperature of exciton and \pm symbol corresponds absorption (+) or emission (-) of phonons. Additionally, in order to better reproduce the shape of the Y1 signature the thermal broadening was taken into account. As a result, the Y1 signature was modeled accounting for

the exciton recombination assisted with either emission or absorption of the Γ_{12}^- phonons (13.6meV) as well as the absorption of the Γ_{15}^- phonons [12–14] as deduced from fitting of the peaks centered at 636, 627, and 609 nm, respectively, in Fig. 4. Notably, the signal correlated with the phonon emission is significantly weaker than that related to the phonon absorption in accordance with the phonon absorption probability to increases as a function of temperature.

4. Conclusion

In conclusion, applying oxygen plasma as a strong oxidant during Cu_2O synthesis, oxygen lean conditions were realized – keeping the oxygen pressure as low as $\sim 10^{-3}$ Pa – remarkably suppressing the formation of V_{Cu} and enabling room temperature exciton luminescence in Cu_2O . Moreover, comparing directly oxidized and MBE grown samples, the V_{O} content was found to be much less critical for excitonic transitions in Cu_2O . As a result, strong room temperature yellow 1s excitonic luminescence was observed and modeled in terms of allowed phonon assisted transitions.

Acknowledgments

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