

Optical bandgap widening of *p*-type Cu₂O films by nitrogen doping

Yoshitaka Nakano,^{a)} Shu Saeki, and Takeshi Morikawa^{b)}

Toyota Central Research and Development Laboratories, Inc., Nagakute, Aichi 480-1192, Japan

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We have investigated the effect of N doping into Cu₂O films deposited by reactive magnetron sputtering. With increasing N-doping concentration up to 3%, the optical bandgap energy is enlarged from ~ 2.1 to ~ 2.5 eV with retaining *p*-type conductivity as determined by optical absorption and Hall effect measurements. Additionally, photoelectron spectroscopy in air measurements shows an increase in the valence and conduction band shifts with N doping. These experimental results demonstrate possible optical bandgap widening of *p*-type N-doped Cu₂O films, which is a phenomenon that is probably associated with significant structural changes induced by N doping, as suggested from x-ray diffraction measurements. © 2009 American Institute of Physics.

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Cuprous oxide (Cu₂O) is a direct-gap semiconductor with a bandgap energy of ~ 2.1 eV and spontaneously shows *p*-type conductivity due to the presence of negatively charged copper vacancies and probably interstitial oxygen.¹⁻³ Cu₂O has been regarded as one of the most promising materials for application in photovoltaic cells because of its high absorption coefficient, nontoxicity, and low-cost producibility.^{4,5} In this case, the general strategy relies on the formation of an electron-hole pair upon absorption of a photon by visible light sensitive Cu₂O. From the same viewpoint of solar energy conversion, Cu₂O can be one of good *p*-type candidates for semiconductor-based photocatalysis and/or photoelectrolysis.⁶⁻⁸ Particularly for the application of solar hydrogen production from water, the energy band structure of *p*-type Cu₂O needs to be modified to position the conduction and valence band edges on optimal levels where the conduction band must be above 0 V versus normal hydrogen electrode (NHE) to produce H₂ with high efficiency, and the valence band must be below +1.2 V versus NHE to produce O₂.⁶ Thus, the modification of the Cu₂O band structure will count for facilitating photoredox processes after the electron-hole formation.

In general, most oxides exhibit poor mobility of holes in the valence band because the O 2*p* states of the upper valence band are localized. Exceptionally, in Cu₂O, the top of the valence band states is derived from fully occupied Cu 3*d* states close to the O 2*p* states and is more mobile when converted into holes.³ Interestingly, *p*-type transparent conductive oxides based on Cu₂O such as CuAlO₂, CuGaO₂, and SrCu₂O₂ have modified energy band structures to reduce oxygen mediated *d-d* coupling between the Cu atoms, resulting in the enlargement of their optical bandgaps.⁹⁻¹¹ Conversely, the top of the valence band of Cu₂O can be narrowed by reducing Cu *d-d* interactions, widening the bandgap. Furthermore, from another standpoint of bandgap engineering, our group has recently reported that the introduction of N as a dopant into substitutional O sites in TiO₂ was effective for optical bandgap modulation of TiO₂-based

photocatalysts.^{12,13} Subsequently, several methods of doping in which nonmetal atoms such as N, S, and C are introduced into the TiO₂ lattice have been reported to shift the absorption edge.¹⁴⁻¹⁶ Combining these concepts, the introduction of N into Cu₂O would be expected as a way to impact on the optical bandgap. Additionally, N is widely accepted as a non-toxic, low-cost, and easily available material, and can be active as an acceptor-type dopant in Cu₂O if it is substitutionally incorporated into the O lattice sites.¹⁷

In this paper, we report on the effect of N doping into Cu₂O films prepared by reactive magnetron sputtering in view of optical bandgap engineering. The N-doped Cu₂O (Cu₂O:N) films used in these experiments were 500 nm thick. They were deposited on glass substrates by radio frequency (rf) reactive magnetron sputtering using a metallic Cu target in a mixture of Ar, O₂, and N₂. Here, the substrate temperature and rf power for sputtering were fixed at 400 °C and 60 W, respectively. The vacuum pressure during the deposition was kept at ~ 1.0 Pa. In order to control N-doping concentration in the Cu₂O:N films, the flow rate of N₂ was varied between 0 and 20 SCCM (SCCM denotes cubic centimeters per minute at STP), retaining that of Ar +1% O₂ mixture gas at 50 SCCM. All the Cu₂O:N samples were confirmed to be polycrystallized by x-ray diffraction (XRD) using Cu *Kα* radiation, as discussed later. Additionally, no XRD peaks assignable to Cu₃N phases were found. From room-temperature Hall effect measurements, all the Cu₂O:N samples showed *p*-type conductivity with hole carrier concentrations in the 10¹⁶ cm⁻³ range, as well as the Cu₂O reference sample. Furthermore, all the samples also showed typical *p*-type photoconductivity in photoelectrochemical measurements in an aqueous solution.

The Cu₂O reference sample without N doping was umber brown, whereas the color of the Cu₂O:N samples changed from umber brown to yellowish green with increasing N₂ flow rate, as shown in Fig. 1(a). These results indicate that N doping may induce any definite variation in energy band structure of Cu₂O films. To investigate N states and to evaluate N-doping concentrations in the Cu₂O:N films, the N 1*s* and O 1*s* core levels on the surface were measured by x-ray photoelectron spectroscopy (XPS) using monochromated Al *Kα* radiation. Assuming that the XPS peak observed at ~ 398.9 eV in the inset of Fig. 1(b) is derived from

^{a)}Present address: Institute of Science and Technology, Chubu University, Kasugai, Aichi 487-8501, Japan.

^{b)}Author to whom correspondence should be addressed. Electronic mail: morikawa@mosk.tytlabs.co.jp.

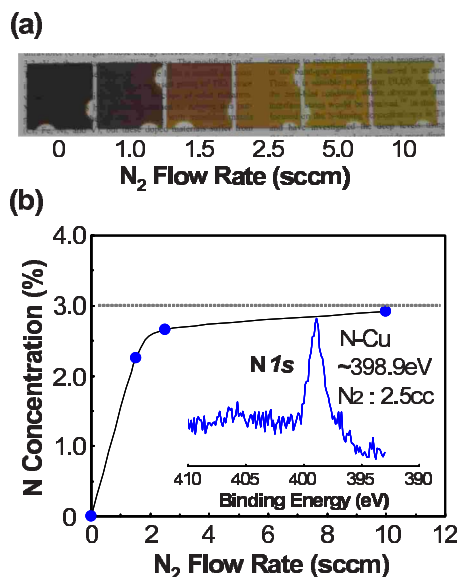


FIG. 1. (Color online) (a) Photographs of Cu₂O:N films prepared under various N₂ flow rates. (b) N-doping concentration in Cu₂O:N films as a function of N₂ flow rate. The inset shows XPS spectrum of N 1s core level for Cu₂O:N film prepared under N₂ flow rate of 2.5 SCCM.

N–Cu bonds formed in the Cu₂O:N films, the N-doping concentrations are determined to be 2.3%, 2.7%, and 2.9% for the Cu₂O:N samples prepared under the N₂ flow rate of 1.5, 2.5, and 10 SCCM, respectively, from the ratio of the peak area at ~398.9 and ~530.5 eV corresponding to the O 1s of O–Cu bonds. Thus, the doping limit of N into Cu₂O is found to be ~3%, as shown in Fig. 1(b).

To estimate optical absorption edges in the Cu₂O:N films, the $(\alpha h\nu)^{1/n}$ versus $h\nu$ curves (Tauc plots) were plotted for different n values ($n=1/2, 3/2, 2, 3$). Here, α is an optical absorption coefficient calculated from absorption spectra and $h\nu$ is an incident photon energy. As shown in Fig. 2(a), in the case of $n=1/2$, all the data show a linear relationship, indicating a direct allowed optical transition in the Cu₂O:N films as well as the Cu₂O reference film. The optical bandgap E_g is determined from the intercept of the straight line portion of the Tauc plots at $\alpha=0$. The E_g value of the Cu₂O film is estimated to be ~2.1 eV, in good agreement with that of bulk crystal. Interestingly, the E_g of the Cu₂O:N films is seen to increase from ~2.1 to ~2.5 eV with increasing N₂ flow rate. So, we can say that the optical bandgap energy strongly depends on the N-doping concentration in the Cu₂O:N films, which is a phenomenon that has yet to be reported for Cu₂O:N films.¹⁷ This increase in E_g of the Cu₂O:N films may be in the same situation as rutile TiO₂ crystals doped with N.¹⁵ From photoelectron spectroscopy in air (PESA) measurements, the ionization energy of the Cu₂O:N films is found to increase from 5.16 to 5.33 eV with an increase in the N₂ flow rate, as shown in Fig. 2(b). Thus, N doping into Cu₂O films can enhance a positive shift in the position of the valence band edge. Here, the conduction band shift ΔE_C of the Cu₂O:N films is estimated from the optical bandgap and valence band shifts ΔE_g and ΔE_V . More interestingly, the conduction band edge is found to be negatively shifted, whose amount is a little more than the ΔE_V . Bandgap diagrams of the Cu₂O and the Cu₂O:N with N-doping concentration of 2.9% are typically shown in Fig. 3. In this case, the ΔE_V and ΔE_C are estimated to be ~0.17 and ~0.23 eV,

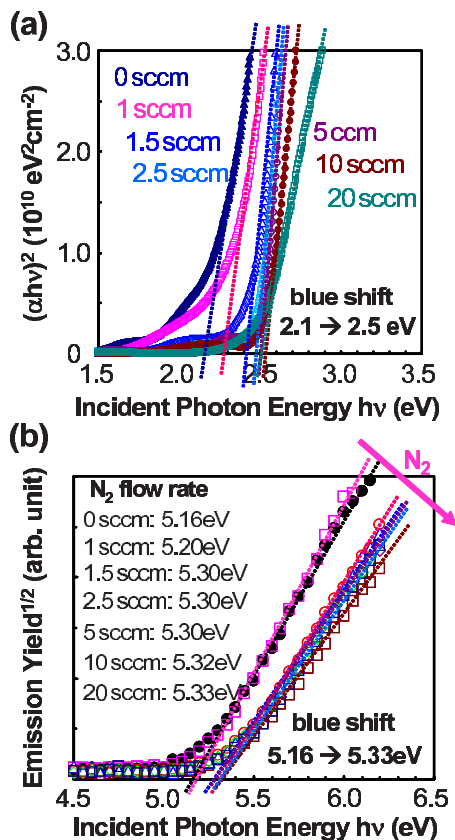


FIG. 2. (Color online) (a) Tauc plots of Cu₂O:N films prepared under various N₂ flow rates. The linear relationship is indicated by dotted lines. (b) PESA spectra of Cu₂O:N films prepared under various N₂ flow rates.

respectively. Both band edge shifts tend to enlarge with increasing N-doping concentration up to ~3%. These experimental results demonstrate possible optical bandgap widening of the Cu₂O films, which is a phenomenon that with repeatability is definitely induced by N doping into Cu₂O films. Strictly speaking, the bandgap widening observed does not monotonically depend on the N-doping concentration and is classified into two stages in view of N doping; in a small N-doping range (N₂ flow rate: 0–2 SCCM), the E_g is largely blueshifted, whereas it tends to be saturated in a heavy N-doping range (N₂ flow rate: >2 SCCM).

Figure 4 shows XRD patterns of the Cu₂O:N films prepared under various N₂ flow rates, together with data of the Cu₂O reference films. The Cu₂O sample shows highly oriented (111) planes. For the Cu₂O:N samples, the peak intensity of the (111) plane is seen to significantly decrease with increasing N₂ flow rate, and (200) planes show up in the heavy N-doping range. More importantly, the (111) peak is shifted in a complicated manner, which is probably classified into two stages in view of N doping; in the small N-doping

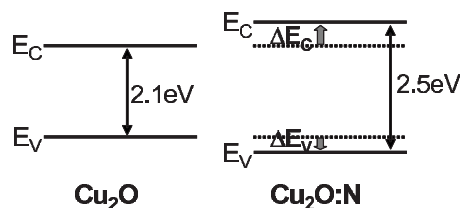


FIG. 3. Energy level diagram of Cu₂O reference film and Cu₂O:N film with N-doping concentration of 2.9%.

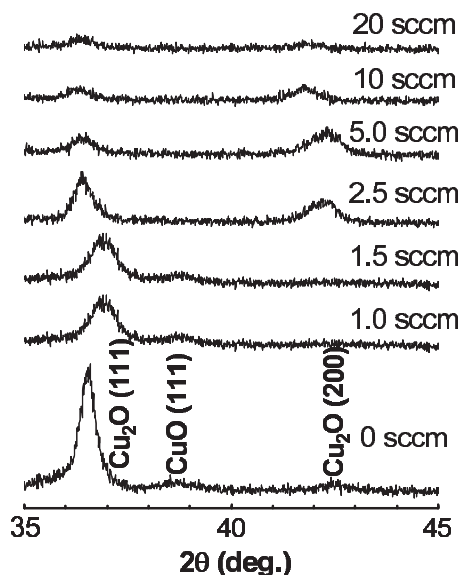


FIG. 4. XRD patterns of $\text{Cu}_2\text{O}:\text{N}$ films prepared under various N_2 flow rates.

range, the peak is largely shifted to the higher angle side compared to that of the Cu_2O reference sample, whereas it is significantly shifted to the lower angle side in the heavy N-doping range. In other words, the (111) plane spacing d_{111} of the $\text{Cu}_2\text{O}:\text{N}$ samples becomes small in the first stage and enlarges in the second stage compared to that of the Cu_2O reference sample. Additionally, the average crystalline size of the $\text{Cu}_2\text{O}:\text{N}$ films was estimated by the Scherrer method based on the (111) peak. The crystalline size decreases from ~ 23 to ~ 15 nm with increasing the N-doping concentration in the small N-doping range, whereas it is almost unchanged (18–20 nm) in the heavy N-doping range.

The optical bandgap widening observed in the $\text{Cu}_2\text{O}:\text{N}$ films is definitely associated with the structural change in Cu_2O induced by N doping rather than size effect because the crystalline size estimated is too large to induce the size effect and the negative ΔE_C is clearly admitted in this study of the $\text{Cu}_2\text{O}:\text{N}$ films.¹⁸ In the small N-doping range, N doping induces a significant decrease in lattice constant d_{111} as revealed from XRD measurements, which indicate the generation of numerous oxygen vacancies. In general, it is difficult for N atoms to replace O atoms in the $\text{Cu}_2\text{O}:\text{N}$ films because the radius of N (1.71) is larger than that of O (1.40). Bearing in mind that the Hall data are little dependent on the N-doping concentration, the sputtering conditions for the $\text{Cu}_2\text{O}:\text{N}$ films in this study may be far from general conditions for acceptor doping of N.¹⁷ Thus, N doping into Cu_2O in this study is considered to artfully generate oxygen vacancies rather than the acceptor doping, which is in reasonable agreement with our previous study of N-doped TiO_2 films.¹³ As a result, the decrease in d_{111} likely leads to the observed

increase in the ΔE_V and ΔE_C . On the other hand, in the heavy N-doping range, the significant increase in d_{111} may induce the generation of another (200) phases from a viewpoint of the energetic stability. So, the d - d interaction between the Cu atoms is considered to become smaller, resulting in enlarging the ΔE_V .^{3,11} Thus, the optical bandgap widening probably proceeds in different mechanisms between the small and heavy N-doping ranges. However, the authentic origin has not been clarified as yet. Conversely, the p -type $\text{Cu}_2\text{O}:\text{N}$ films equipped with various conduction and valence band edges are of great worth as one of promising p -type semiconductors for semiconductor-based photocatalysis and/or photoelectrolysis. These experimental findings in this study and their further detailed investigations are likely to provide important information on materials design where a p -type and a n -type semiconductors are coupled to drive photoreductions and photo-oxidations for a two-step excitation process such as solar hydrogen production from water.¹⁹

In summary, we have demonstrated possible optical bandgap widening of p -type Cu_2O films by N doping based on optical absorption and PESA measurements. This phenomenon is probably associated with the structural change in Cu_2O induced by N doping, as suggested from XRD measurements.

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