Probing Defects in Nitrogen-Doped Cu$_2$O

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Nitrogen doping is a promising method of engineering the electronic structure of a metal oxide to modify its optical and electrical properties; however, the doping effect strongly depends on the types of defects introduced. Herein, we report a comparative study of nitrogen-doping-induced defects in Cu$_2$O. Even in the lightly doped samples, a considerable number of nitrogen interstitials (Ni) formed, accompanied by nitrogen substitutions (NO) and oxygen vacancies (VO). In the course of high-temperature annealing, these Ni atoms interacted with VO, resulting in an increase in NO and decreases in Ni and VO. The properties of the annealed sample were significantly modified as a result. Our results suggest that Ni is a significant defect type in nitrogen-doped Cu$_2$O.

Coprus oxide (Cu$_2$O), a p-type semiconductor with a direct band gap of 2.1 eV, has long been considered a promising material for low-cost solar-energy conversion and photocatalysis$^{1-5}$. Its advantages include a high absorption coefficient, a suitable band-gap width, chemical stability, non-toxicity and abundant reserves. Nitrogen doping in Cu$_2$O is an important research topic because of its tremendous potential for overcoming the major disadvantage of Cu$_2$O - its high resistance. Moreover, recent research has revealed that in addition to conductivity improvement, nitrogen-doped Cu$_2$O, hereafter referred to as Cu$_2$O:N, exhibits enhanced light absorption below the band gap, most likely because of the introduction of an intermediate band (IB) located $\sim$0.7 eV above the valence band maximum (VBM)$^{6,7}$. Its advantageous band gap and IB level have made Cu$_2$O:N an excellent candidate material for IB solar cells$^8$. Its enhanced subband absorption in combination with its excellent visible-light absorption is also an outstanding advantage for photocatalysis because most inorganic photocatalysts suffer from poor activity or even inactivity under visible-light illumination, including the extensively studied TiO$_2$ and perovskite compounds$^{9-11}$. However, several other groups have observed no enhancement in subband absorption even in heavily doped Cu$_2$O:N films$^{12,13}$, and Nakano et al. even observed a band-gap-widening effect upon nitrogen doping$^{14}$.

Through the application of first-principles calculations, several theoretical investigations of Cu$_2$O:N have also been performed. Li et al. claimed that nitrogen impurities in Cu$_2$O induce a marked widening of the band gap when oxygen vacancies are present$^{15}$, which could account for the experimentally observed optical band-gap widening of Cu$_2$O:N prepared via the sputtering technique$^{14}$. Conversely, Zhao et al. reported a theoretical prediction that nitrogen doping should slightly widen the band gap, causing the formation of an IB in the gap located at $\sim$0.9 eV above the VBM$^{14}$.

In general, there is still some controversy regarding the effects of nitrogen doping on Cu$_2$O, and no comprehensive understanding has yet been reached. It is well known that impurities at different sites in the lattice have distinct effects on the electrical and optical properties of a material$^{8,10}$. However, interstitial nitrogen (N$_i$) in Cu$_2$O has long been ignored in previous experimental and theoretical studies, which have focused only on nitrogen impurities substituted at oxygen sites (N$_O$)$^{8,9,12,13,15-19}$. In this work, we found that even in the lightly doped samples, a considerable number of N$_i$ formed in Cu$_2$O, along with N$_O$ and oxygen vacancies (V$_O$). In the course of annealing, migrating N$_i$ reacted with V$_O$ forming more N$_O$, thereby altering the corresponding contents of these point defects and resulting in a significant change of the optical and electrical properties of the material.

Results

Cu$_2$O and Cu$_2$O:N films were obtained via the post-oxidation of Cu (111) films that were initially deposited on c-plane Al$_2$O$_3$ buffered with a 400 nm thick, semi-insulating ZnO film$^{20}$. Nitrogen doping was achieved by
introducing a nitrogen plasma through a radio-frequency (RF) plasma gun during the oxidation process. It was found that a micro-zone phase separation occurs when fabricating Cu$_2$O films at high temperatures, while oxidizing at 300°C resulted in single oriented Cu$_2$O (111) films. So that this recipe was adopted for all samples used in this study. Figure 1(a) presents typical XRD 0-2θ scans for the samples. Only one peak corresponding to the Cu$_2$O (111) plane can be observed, in addition to the ZnO (0002) and Al$_2$O$_3$ (0006) signals; these results are consistent with the in situ reflection high-energy electron diffraction (RHEED) observations, as shown in Figure 1(b). Thus no traces of CuO, Cu or Cu$_3$N phases were found, suggesting high quality Cu$_2$O with diluted nitrogen in the doped samples. The clear RHEED patterns also indicate the fine crystallinity of the films. Atomic force microscopy images (not shown) revealed a uniform surface with a root-mean-square roughness of ~10 nm in a scan area of 10 μm × 10 μm.

The resistivities of the as-grown Cu$_2$O and Cu$_2$O:N samples were approximately 340 Ω·cm and 100 Ω·cm, respectively, measured by Hall effect. The carrier density and mobility of the Cu$_2$O were 3.5 × 10$^{16}$ cm$^{-3}$ and 53 cm$^2$V$^{-1}$s$^{-1}$, respectively. Interestingly, the Cu$_2$O:N sample demonstrated ambiguous p-type conduction behavior (Fig. S1 in the supplementary information), suggesting a low value for the Hall coefficient and/or the existence of hole traps. Annealing were applied to activate nitrogen related acceptors and/or remove the hole traps.

Figure 2(a) shows room temperature values for the hole density, mobility and resistivity of the Cu$_2$O and Cu$_2$O:N samples after annealing at 750°C for 10 min as functions of the nitrogen plasma power. A power of 0 W represents undoped Cu$_2$O. It is clear that the hole density increased with the power of the nitrogen plasma (likely to be proportional to the doping level) and the mobilities of Cu$_2$O:N were all smaller than those of Cu$_2$O (also consistent with the hypothesis of high nitrogen incorporation). The hole concentrations of Cu$_2$O:N were in the range of 10$^{16}$ cm$^{-3}$, i.e. two orders of magnitude higher than that of Cu$_2$O$^{21}$-23. Figure 2(b) presents the room temperature Hall data for Cu$_2$O:N synthesized using nitrogen plasma power of 200 W, as a function of annealing temperature. The lowest resistivity and the highest hole density were obtained upon annealing at 750°C. When the sample was annealed at 800°C, although the mobility was higher because of the improved crystal quality, the hole density decreased, leading to reduced conductivity. A possible explanation is that annealing at such a high temperature may also induce the out diffusion of nitrogen in addition to the acceptor activation. Note that the annealing conditions can be further optimized for better conductivity; nevertheless, in our study, the results indicated that the samples annealed at 750°C were already suitable for the study of nitrogen-related defects on behalf of the prominent evolution in electrical properties. Furthermore, the temperature-dependent hole concentration was also measured to determine the activation energy of the dominant acceptors in Cu$_2$O:N, which was calculated to be 121 meV (supplementary information). This level is attributed to extrinsic N$_O$ acceptors, because the only reasonable alternative of copper vacancies (V$_{Cu}$) exhibits a much deeper level$^{21-23}$. Figure 3 presents the nitrogen concentration versus depth profiles of the Cu$_2$O:N films doped with 200 W nitrogen plasma as measured by secondary ion mass spectroscopy (SIMS), which confirms: (i) nitrogen incorporation into our films and (ii) its gradual out diffusion during anneals.

**Discussion**

The data in Fig. 2 and Fig. 3 suggest that nitrogen, likely in favor of N$_O$, behaves as an efficient acceptor in Cu$_2$O:N. Logically, to enhance the conductivity of Cu$_2$O:N, we simply need to increase the doping level and/or optimize the annealing process to balance the activation and outward-diffusion processes. However, the microscopic picture of the doping mechanism is still not clarified. N$_O$ is likely not the only defect type introduced by nitrogen doping. As is well known, when aliovalent substitutions occur in ionic compounds, a charge-compensation mechanism is required to ensure that the overall charge remains neutral. For Cu$_2$O:N with ionized N$_O$ acceptors, the compensation can be achieved, e.g. through the formation of anion vacancies (V$_O$) or less likely, cation interstitials (Cu$_i$) though their formation energy is relatively high$^{21,22}$.

Photoluminescence (PL) is a non-destructive technique for the investigation of defects in semiconductors. The PL spectrum of Cu$_2$O has been adequately researched in the literature, and the luminescence related to excitons, V$_O$, and Cu$_i$ has been well established$^{24-26}$. However, previous research has not produced sufficient results with respect to PL studies of Cu$_2$O:N. Ishizuka et al. have reported that Cu$_2$O:N exhibits no PL peak prior to hydrogen or crown-ether cyanide treatment, indicating the existence of non-radiative recombination centers in the polycrystalline Cu$_2$O$^{18,19}$.

Figure 4(a) presents the PL spectra of the Cu$_2$O samples, with arrows indicating positions related to the excitons, V$_O$ and Cu$_i$. The presence of V$_O$ is due to the oxygen-lean growth conditions. After high-temperature annealing, the exciton luminescence was remarkably enhanced, whereas the intensity of the V$_O$ signature did not change significantly, suggesting an improvement in crystal quality after annealing. Notably, the formation of V$_Cu$ was suppressed because of the oxygen-lean conditions during growth, enabling a strong exciton luminescence$^{25,26}$. The shape of the exciton luminescence peak can be well interpreted in terms of phonon-assisted transitions, as discussed in Ref. 26.

Figure 4(b) presents the spectra of the Cu$_2$O:N films while the spectrum of the Cu$_2$O sample annealed at 750°C is also included as a reference. The most distinguishable features are the suppressed
Exciton luminescence and intense VO-related luminescence of the Cu$_2$O:N films after annealing, supporting our hypothesis that incorporation of nitrogen is associated with the VO generation. Concurrently, it has been demonstrated that the presence of VO has no responsibility for damping the exciton luminescence$^{25,26}$, suggesting other traps to be involved and specifically Ni and NO may be considered as prime candidates for non-radiative recombination mechanisms.

Indeed, the exciton luminescence was slightly enhanced (see Fig. 4(c)), whereas the intensity of the VO signal, in contrast, decreased with increasing annealing temperature. Taking into account the fact that PL intensities are proportional to defect contents, the evolution of the VO signature suggests that the annealing processes somehow reduced the VO content in the Cu$_2$O:N samples. It should be mentioned that the as-grown Cu$_2$O:N sample is likely to contain the highest density of VO; however, this fact was not directly reflected by the PL intensity because of the poorer crystallinity of the as-grown sample. Considering that the annealing process played a limited role in repairing the VO in the undoped Cu$_2$O (see Fig. 4(a) and Ref. 26), this trend of decreased VO concentration in Cu$_2$O:N should be attributed to the evolution of defects not available in the undoped films. A reasonable explanation is the refilling of VO by interstitial atoms, likely Ni, which move faster at higher temperatures and thus can more easily occupy the vacancy sites. Interstitial oxygen (O$_i$) is another possible candidate to react with VO; however, its formation is disfavored under oxygen-lean growth conditions$^{21,22}$. Thus, the difficulty encountered in judging the conduction type of the as-grown Cu$_2$O:N based on the Hall measurements is the natural result of the presence of less N$_i$ and more N$_i$ in the film.

Further evidence for Ni is observed in Figure 4(c), the enlarged spectra of the Cu$_2$O:N films in the vicinity of the exciton level. The as-grown Cu$_2$O:N sample exhibited a unique signature located at 652 nm (1.90 eV). This signal did not originate from the $\beta$ band in nonstoichiometric Cu$_2$O, despite the very similar energy level (1.91 eV) because the $\beta$ band created by exciton-defect complexes would not be affected by the annealing process$^{27,28}$. It cannot be related to NO; if it were, it would not have disappeared after annealing. Therefore, this 652 nm peak is most likely attributable to the emission related to Ni. The absence of this signature in the annealed samples is the result of the diffusion of nitrogen out of the material and the transformation of Ni into NO. This interpretation is reasonable, considering the variation in the VO signature and the electrical properties.

It is worth noting that for all our samples, no signature could be observed at approximately 680 nm (Fig. 4(b)), where Ishizuka et al. observed a lone peak in the PL spectrum of Cu$_2$O:N after passivation treatment$^{18,19}$. Park et al. have also reported the observation of this 680 nm luminescence signature in Cu$_2$O films without intentional doping$^{29}$, indicating that the origin of this feature in polycrystalline Cu$_2$O thin films remains uncertain.

In order to extend our interpretation, we applied X-ray photoelectron spectroscopy/X-ray Auger electron spectroscopy (XPS/XAES) to probe the defects$^{30-32}$. A comparative study was conducted using four samples – two as-grown and two 750 °C annealed samples of Cu$_2$O and Cu$_2$O:N, labeled as Cu$_2$O, Cu$_2$O AN, Cu$_2$O:N, and Cu$_2$O:N AN, respectively. Notably, the confirmation of the nitrogen atoms' locations from their chemical states or bonding status is impractical because no signal related to nitrogen could be detected because of the low doping level ($\sim 10^{18}$ cm$^{-3}$). Instead, we relied on
the detection of other defects to interpret the formation and evolution of nitrogen-related defects by means of the defects’ interactions.

Figure 5 presents the high-resolution XPS spectra of the (a) Cu2p and (b) O1s core levels. As shown in Fig. 5(a), the Cu-related peaks exhibit a symmetric shape with no satellite structure at approximately 943 eV, ruling out the presence of Cu2+ in these films. The fitting of the Cu2p3/2 peaks indicates a binding energy of 932.6 eV, corresponding to that of Cu in Cu2O. The presence of metallic Cu clusters may also be ruled out accounting for: (i) the Cu2p peaks exhibit strong symmetry, and the full widths at half maximum (FWHM) for all different samples are nearly identical (1.43–1.49 eV); (ii) the XRD results show no evidence of Cu (Fig. 1); and (iii) the samples exhibited good p-type conductivity. Further, the signatures of the O1s peaks at 530.4 eV are consistent with O-state in Cu2O too. Notably, a much more pronounced variation in the FWHM values (1.15–1.58 eV, see Fig. 5(b)) indicates a trend that may be correlated with the presence of VO based on literature interpretations of oxygen deficient samples30,31.

As XAES is much more sensitive to the nature of the neighboring bonds and/or point defects than XPS30,32, the evolution of Cu LMM Auger lines was measured and Fig. 6 shows typical Cu-related signatures deconvoluted with five different components. Notably, three peaks located at 913.5 eV, 919.5 eV and 921.4 eV are known not to be sensitive to the chemical environment33–35. The dominating peaks in Fig. 6 at 916.8 eV (labeled as peak 1) and 918.3 eV (labeled as peak 2) are typically attribute to Cu2O and Cu, respectively, though peak 2 can also be observed in nonstoichiometric Cu2O33,34. In fact, the appearance of peak 2 in Fig. 6 is intriguing since we have ruled out the presence of Cu, or Cu cluster in our films. An alternative identification of peak 2 may be to assign it to VO, since strong localized unpaired electrons of copper atoms neighboring VO might influence its effective charge state readily detectable by XAES21,22,30. In another words, the signal of Cu next to VO (-O-Cu-V_O), i.e. Cu dangling bond, is distinguishable from Cu2+ (-O-Cu-O), assuming that one VO would lead to an “aggregation” of four Cu atoms (Fig. S3 in the supplementary information).

Adopting this identification, further conclusions may be done considering the evolution of the peaks intensities in Fig. 6. Notably, the annealing results in much more pronounced decrease of the VO content (in terms of the integrated intensity ratio of peak 1 and peak 2) in Cu2O:N, comparing to that in Cu2O, which is consistent with the PL results, altogether suggesting a critical role of Ni to interact with VO in the course of annealing. Indeed, during annealing, the supply of atmospheric oxygen is insufficient to change VO concentration drastically, while the presence of Ni in Cu2O:N makes the major contribution to interact with VO forming NO.

The higher ratio of the annealed Cu2O:N sample indicates the lower VO content, i.e., fewer Cu dangling bonds, compared with the annealed Cu2O sample; this finding reflects the important influence of the growth conditions, as the nitrogen plasma provided additional total anions. One may argue that this result seems to be in conflict with the stronger VO-related luminescence of Cu2O:N, as shown in Figure 5(b). We attribute this phenomenon to the passivation effect of nitrogen36, which arises because Ni can also move to defect sites other than VO. This passivation effect is further evidence of significant Ni formation induced by doping. Ishizuka et al. also observed an enhanced PL intensity after nitrogen doping18.

Notably, the fitted FWHMs of peak 1 for the Cu2O:N samples (Table 1) are slightly broadened compared with those of the undoped Cu2O samples. Fixing the FWHMs of peak 1 yielded very similar

![Figure 4](https://www.nature.com/scientificreports/articles/doi:10.1038/srep07240/srep07240_f4.png)

**Figure 4** | Photoluminescence spectra of (a) Cu2O samples, (b) Cu2O:N samples doped at 200 W, and (c) enlarged portion of (b) in the vicinity of the exciton emission.

![Figure 5](https://www.nature.com/scientificreports/articles/doi:10.1038/srep07240/srep07240_f5.png)

**Figure 5** | XPS (a) Cu 2p spectra, and (b) normalized O 1s spectra of Cu2O and Cu2O:N samples.
Methods

The samples were fabricated in an ultra-high-vacuum chamber with a background pressure within the lower range of $10^{-7}$ Pa. A conventional Knudsen cell was used to evaporate metallic Cu (6N). Cu (111) films were initially deposited on c-plane Al$_2$O$_3$, buffered with a 400 nm thick semi-insulating ZnO (0001) film. Cu$_2$O films were obtained via post-oxidation using oxygen plasma, and Cu$_2$O:N films were obtained under similar conditions through co-treatment with oxygen and nitrogen plasmas. Specifically, the oxygen plasma was used at a fixed O$_2$ flux of 1 sccm (the partial pressure was maintained within the lower range of $10^{-3}$ Pa), and discharged via RF power. The doping level was controlled by varying the RF power and the N$_2$ flux. The thickness of the prepared films was approximately 150 nm. The oxidation/doping temperature was 300 ºC for all samples. The typical oxidation time was approximately 90 minutes. The oxidation process was monitored by means of in situ reflection high-energy electron diffraction (RHEED) observations. Once the RHEED pattern indicated complete oxidation of Cu into Cu$_2$O, the plasma exposure was terminated.

Table 1 | Summary of the Cu LMM peak-fitting parameters

| Sample   | Peak | K.E. [eV] | Intensity | FWHM [eV] | Intensity ratio |
|----------|------|-----------|-----------|-----------|----------------|
| Cu$_2$O  | 1    | 916.8     | 19252.42  | 2.10      | 2.56           |
|          | 2    | 918.3     | 7519.22   | 1.52      |                |
| Cu$_2$O AN | 1  | 916.7     | 22386.8    | 2.10      | 3.61           |
|          | 2    | 918.3     | 6193.66   | 1.52      |                |
| Cu$_2$O:N | 1   | 916.8     | 12843.29  | 2.30      | 2.43           |
|          | 2    | 918.3     | 5276.19   | 1.52      |                |
| Cu$_2$O:N AN | 1 | 916.8     | 18128.31  | 2.20      | 6.83           |
|          | 2    | 918.3     | 2655.39   | 1.52      |                |

Shorter or longer treatment times would result in undesired phases of Cu and Cu$_2$O, respectively. More details can be found in our previous report.

Several samples were subjected to post-annealing in the same chamber under an oxygen-gas atmosphere (also at $10^{-7}$ Pa) at various temperatures. The temperature ramping rate was 30 ºC min$^{-1}$. Once the set temperature was reached, that temperature was maintained for 10 min, and the sample was then cooled at the same rate of 30 ºC min$^{-1}$.

XRD measurements were performed using a Mac Science M18XHF diffractometer with a Cu Kα radiation source ($λ = 1.5406$ Å) at 40 kV and 50 mA (2 kW).

The van der Pauw configuration was used for the Hall measurements. Room-temperature tests were performed using an Ecopia HMS-3000 system, and the results were double-checked using a home-made Hall system. The Hall coefficient was extracted from the trace curve of the transverse voltage recorded using an alternating magnetic field and a constant current (supplementary information). The temperature-dependent hole density was recorded using a Lakeshore model 7604 Hall system. The acceptor level was extracted using the following equation:

$$p = \frac{N_d - N_v}{2N_D} \exp\left(\frac{-E_a}{kT}\right)$$

where $N_d$, $N_v$, $N_D$, $E_a$, $k$, and $T$ are the acceptor density, donor density, effective density of states in the valence band, acceptor level, Boltzmann constant, and absolute temperature, respectively, and

$$N_i = 2\left(2m_hkT/h\right)^{1/2}$$

where $m_h$ and $h$ are the hole effective mass and the Plank constant, respectively.

For the photoluminescence measurements, the samples were excited using a 532 nm laser at 1 mW focused to a spot of approximately 2 μm. The spectra were measured at room temperature in a back-scattering geometry. The integration time was 10 seconds in all cases.

SIMS measurements were performed using a Cameca IMS 7f microanalyzer. XPS measurements were performed using a PHI-5300 ESCA Spectrometer with a monochromatic Al K$_x$ X-ray source at 1486.6 eV. All data were collected at a nominal depth of 6 nm after Ar- ion sputtering, and the damage effect proved to be negligible (supplementary information). Spectral analysis was performed using XPSPeak version 4.1. Shirley background subtraction was adopted, and the fitting results were determined based on the minimum standard deviation.

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