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## Extra-low resistivity in N and H doped Cu<sub>2</sub>O thin films grown by room temperature RF sputtering

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Cuprous oxide (Cu<sub>2</sub>O) is an intrinsic p-type semiconductor representing an interesting, potential hole transporting material in 3rd generation solar cells. However, its practical applications are significantly limited by its intrinsically high resistivity. In the present study, we show that polycrystalline Cu<sub>2</sub>O thin films with an extra-low resistivity of 0.16 Ω cm can be grown by radio frequency (RF) sputtering by exploiting the effects of nitrogen and hydrogen doping. Significantly and differently from previous studies, the films are deposited at room temperature and the material doping is performed through the simultaneous introduction of both dopants in the Cu<sub>2</sub>O films during the growth process. The effects of N and H dopants on the Cu<sub>2</sub>O properties are investigated by performing resistivity, Hall effect, UPS, X-ray Diffraction and Raman measurements on a pristine Cu<sub>2</sub>O film, on Cu<sub>2</sub>O films doped with N and H individually, as well as on films containing both dopants. Such a systematic investigation of the doping effects permits to perform a comparative analysis of the achieved results and data from literature and to develop an exhaustive, interpretative framework that clarifies the role of native defects and N and H dopants in reducing the resistivity of Cu<sub>2</sub>O.

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### 1. Introduction

Cuprous oxide, Cu<sub>2</sub>O, is a spontaneous p-type semiconductor characterized by a direct bandgap in the range of 1.9 eV and 2.6 eV, and a high absorption coefficient of 10<sup>6</sup> cm<sup>-1</sup>.<sup>1</sup> Owing to its non-toxic nature and low production cost, Cu<sub>2</sub>O has attracted considerable interest for applications in optoelectronic devices. Over the past decades, extensive research has focused on the use of Cu<sub>2</sub>O as an absorption layer in thin-film solar cells, as the theoretical power conversion efficiency (PCE) of Cu<sub>2</sub>O-based solar cells has been estimated to approach 20%.<sup>1,2</sup> However, despite this promising theoretical potential, the highest energy conversion efficiency of Cu<sub>2</sub>O based solar cells reported so far is still below 10%.<sup>3–5</sup> With the advent of perovskite materials for the 3rd generation solar cells, whose efficiency surpassed the 27%, Cu<sub>2</sub>O loosed interest as an absorbing material. Instead, its p-type nature made this oxide interesting as a hole transporting layer (HTL) since the currently used material in planar perovskite solar cells, the SpiroMeOTAD, suffers from high cost and limited long-term stability. Beyond its favorable electrical

properties, Cu<sub>2</sub>O represents a promising HTL alternative due to its suitable energy-level alignment with a wide range of perovskite materials.<sup>6–8</sup> The intrinsic, p-type Cu<sub>2</sub>O conductivity is generally attributed to the presence of copper vacancies, which show an acceptor character and easily form thanks to their low formation energy.<sup>9–11</sup> Recent theoretical calculations have shown that copper vacancies may form in a normal configuration, V<sub>Cu</sub>, and a split configuration, V<sub>Cu,split</sub>, with similar formation energies. These two vacancies induce electronic energy levels located at ~0.2 eV and 0.4–0.5 eV from the valence band maximum (VBM), respectively.<sup>10,12</sup> In particular, values of 0.22 eV and 0.47 eV above VBM have been reported by Scanlon *et al.* for V<sub>Cu</sub> and V<sub>Cu,split</sub>,<sup>12</sup> in a close agreement with measured values of 0.2 eV and 0.5 eV reported by Paul *et al.*,<sup>8</sup> and 0.22 eV and ~0.4 eV reported by Nyborg *et al.*,<sup>10</sup> respectively. These results indicate a weak shallow and a deep acceptor character for the two vacancy configurations, respectively, which explain why the native p-type doping leads to low hole concentrations in Cu<sub>2</sub>O films. This moderate p-type character implies that the pristine Cu<sub>2</sub>O resistivity is too high for its exploitation in optoelectronic devices, *e.g.*, most reported resistivity values are higher than 1 Ω cm. Lower resistivity values are mainly obtained by nitrogen doping, which is the most undertaken route for a resistivity lowering.<sup>13–20</sup> Nitrogen could be introduced in the Cu<sub>2</sub>O lattice as an oxygen substitute, N<sub>O</sub>, or in the molecular form when an N<sub>2</sub> molecule occupies a V<sub>Cu</sub> site, (N<sub>2</sub>)<sub>Cu</sub>. Recent theoretical calculations indicate N<sub>O</sub> as a deep

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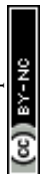


acceptor (inducing an energy level at 0.5 eV above VBM) and  $(N_2)_{Cu}$  as a shallow acceptor (inducing a level at about 0.2 eV above VBM).<sup>21</sup> These results fully agree with those of electron energy loss spectroscopy measurements which show the presence of nitrogen in the molecular form and rule out that of  $N_O$  in  $Cu_2O$  thin films showing improved electron mobility and resistivity values.<sup>22</sup>  $Cu_2O$  nitrogen doping was also investigated by performing nitrogen ion implantation.<sup>23</sup> In that study, a shift of the Fermi level towards the valence band maximum was observed, thus fully confirming the nitrogen acceptor behavior. To the best of our knowledge, low resistivity values ( $<1 \Omega \text{ cm}$ ) in nitrogen doped  $Cu_2O$  were obtained by Wang *et al.*,<sup>22</sup> (0.8  $\Omega \text{ cm}$ ) in film grown at room temperature, and by Rezek *et al.* (0.05  $\Omega \text{ cm}$ ) in films grown at 190 °C.<sup>17</sup> A resistivity value of 0.4  $\Omega \text{ cm}$  was also obtained for  $Cu_2O$  films grown at 260 °C by atomic layer deposition with  $N_2$  as the carrier gas by Sekkat *et al.*<sup>18</sup>  $Cu_2O$  hydrogen doping was also reported.<sup>10,24–28</sup> In this regard, first studies investigated the effects induced by post-growth hydrogenation treatments on the properties of  $Cu_2O$  and N doped  $Cu_2O$  polycrystalline films.<sup>25,26,28</sup> These studies reported a decrease of the hole density and an increase of Hall mobility and resistivity in hydrogenated  $Cu_2O$ , possibly induced by a H passivation of oxygen dangling bonds (O-DB's) present in acceptor defects (as in the case of the  $V_{Cu}$ 's). Instead, in the case of hydrogenated N doped films, an increase of the hole density and a decrease of Hall mobility and resistivity were explained by proposing a H passivation of donor defects possibly involving Cu-DB's. A subsequent, theoretical study accounted for those experimental findings by showing that interstitial H in  $Cu_2O$  behaves as a deep amphoteric impurity able to compensate both shallow acceptors and donors.<sup>29</sup> Moreover, regarding the H interaction with acceptor defects, the same study showed that hydrogen can form H- $V_{Cu}$  complexes with low formation energy where the H atoms bind to O-DB's.<sup>29</sup> These complexes induce an ultra-deep acceptor level at about 1.2 eV above the VBM, thus neutralizing the  $V_{Cu}$  acceptor effect (this result was supported by a subsequent experimental study on defects in single crystal  $Cu_2O$ <sup>10</sup>). A similar hydrogen effect is expected in the case of O-DB's belonging to acceptor defects which may occur at the grain boundaries in polycrystalline  $Cu_2O$ . The investigation of H interaction with shallow donors is instead somewhat lacking. The same theoretical study showed that, despite the presence of Cu-DB's in the oxygen vacancy,  $V_O$ , this defect does not behave as a donor. Moreover, a H atom interacts with a  $V_O$  by occupying the O site and forming an amphoteric  $H_O$  defect. No indications were given instead on a possible passivation of Cu-DB's and related donor defects occurring inside, or at the boundaries of, the grains of  $Cu_2O$  films. Such a lack of information was somewhat compensated by a subsequent study, where, differently from the above-mentioned studies, hydrogen was introduced during the RF sputtering growth of undoped  $Cu_2O$  films.<sup>24</sup> As a further peculiarity of this study, the growth process was performed at high temperatures. This induced an increase of the grain size and a H accumulation at the grain boundaries of the

polycrystalline films. The same study reported an increase of Hall mobility and a decrease of resistivity together with a negligible change of the Hall carrier density. These results were explained by showing that H passivated donor defects at the grain boundaries without affecting the acceptor defects present inside the single grains. Finally, in a recent study, the effects of H implantation in undoped  $Cu_2O$  films were investigated.<sup>27</sup> This study showed that H can passivate both acceptors and donors. Overall, the above results gave important indications by showing that generally H can compensate/passivate acceptor and donor defects occurring at the boundaries of, or inside, the grains of  $Cu_2O$  films, thus affecting the carrier mobility, the carrier densities, and the resistivity values. As a final note, in undoped  $Cu_2O$  films deposited in the presence of  $H_2$  gas as well as in films subjected to post-growth H treatments, the achieved resistivity values were higher than 1  $\Omega \text{ cm}$ .<sup>24–26,28</sup> In the present work, it is shown that a remarkable extra-low resistivity of 0.16  $\Omega \text{ cm}$  can be achieved in N and H doped thin  $Cu_2O$  films grown by reactive sputtering deposition. Two features distinguish the present approach from the above-mentioned ones: the two dopants are simultaneously introduced in the  $Cu_2O$  films during the growth process and the growth is performed at room temperature. The effects of N and H doping on the  $Cu_2O$  properties have been investigated by performing resistivity, Hall effect, XRD, UPS (ultraviolet photoelectron spectroscopy), and Raman measurements on four different kinds of samples: pristine  $Cu_2O$ , H doped  $Cu_2O$  ( $Cu_2O:H$ ), N doped  $Cu_2O$  ( $Cu_2O:N$ ), and H and N doped  $Cu_2O$  ( $Cu_2O:N/H$ ). Such a systematic investigation of the effects induced by each dopant has permitted to perform a comparative analysis of the achieved results and data from literature and to draw a consistent, interpretative picture explaining the role of the native defects as well as of the N and H dopants in the resistivity reduction.

## 2. Experimental

Pure, H doped, N doped, and H and N doped  $Cu_2O$  thin films, with thickness of 50 nm, were deposited by reactive radio-frequency (RF) magnetron sputtering, employing a Meivac MAK multisource equipped with  $3 \times 2''$  confocal sputter sources. Prior to each deposition, the chamber was evacuated to a base pressure of  $6.2 \times 10^{-6}$  mbar. The soda lime silica glass substrates of  $2.5 \times 2.5 \text{ cm}^2$  were placed at 4 cm from the  $Cu_2O$  target (99.99%, purity) and maintained at room temperature throughout the process. During the deposition the working pressure and the RF power were  $6 \times 10^{-3}$  mbar and 25 W, respectively. The N and H doping were realized by adding  $N_2$  or an Ar +  $H_2$  mixture to Ar gas. Field emission scanning electron microscopy ZEISS SIGMA 300 and energy dispersive spectroscopy (EDS) equipped with an Xplore 30 mm<sup>2</sup> EDS detector (Oxford Instruments, UK), were employed to estimate the N content of  $Cu_2O:N$  and  $Cu_2O:N/H$  thin films using the Oxford Instruments AzTec Software. XRD measurements were conducted using a Panalytical Empyrean diffractometer in



Bragg–Brentano geometry. The system employed a Cu X-ray tube ( $K\alpha_1 = 1.54060 \text{ \AA}$ ,  $K\alpha_2 = 1.54443 \text{ \AA}$ ) as the radiation source and a PixCel 3D detector operating in linear mode for signal detection. The incident beam was conditioned using divergent slits ( $1/4^\circ$ – $1/2^\circ$ ), and diffraction patterns were recorded over a  $2\theta$  range of  $5^\circ$  to  $70^\circ$ . Due to the extremely weak diffracted intensity, each scan required an extended acquisition time of 7 hours. Micro-Raman measurements were performed by a Renishaw inVia spectroscope. 200 acquisitions per point were collected with a 457 nm laser source, setting the laser power at 10% and time exposure at 1 s in order to avoid surface damage. Resistivity, carrier concentration, and mobility were measured by using the four-point probe method as well as a Hall effect measurement system with a 1.1 T electromagnet in the Van der Paw geometry. UPS measurement were performed with angle resolved ultraviolet photoemission spectroscopy (ARUPS). Spectra were recorded in a Vacuum Generators VG-450 ultrahigh-vacuum chamber at a pressure of less than  $2.6 \times 10^{-10}$  mbar. Unpolarized 21.2 eV radiation from a helium discharge lamp was used. The estimated total energy resolution as determined by the analyzer voltages and the width of the He I light was 100 meV, the angular resolution of the hemispherical analyzer was  $\pm 1^\circ$ .

### 3. Results and discussion

#### 3a. Electrical and optical characterizations

Electrical measurements were preliminarily performed in pure  $\text{Cu}_2\text{O}$  samples and in a set of doped samples obtained varying the concentration of gases in the mixtures. The optimal mixture compositions, which permit to grow  $\text{Cu}_2\text{O}$  films with minimum resistivity, correspond to a 40% of  $\text{N}_2$  in the  $\text{N}_2/\text{Ar}$  mixture and a 0.35% of  $\text{H}_2$  in the  $\text{H}_2/\text{Ar}$  and  $\text{H}_2/\text{N}_2/\text{Ar}$  mixtures. The samples showing minimum resistivity values were selected for all the here performed investigations. The corresponding resistivity, carrier concentration, and mobility values are reported in Table 1. The Hall measurements confirm the p-type character of all of the investigated samples and show a progressive increase of the hole concentration on going from the  $\text{Cu}_2\text{O}$  to the  $\text{Cu}_2\text{O:N/H}$  samples. Such an increase is in agreement with the observed, progressive reduction of the hole mobility, which is generally attributed to scattering on neutral and ionized defect centers.<sup>10</sup>

The N content in the  $\text{Cu}_2\text{O}$  samples were estimated by performing EDS measurements. Table 2 reports the Cu/N atomic ratio measured for four sets of N and N/H doped  $\text{Cu}_2\text{O}$  films

**Table 1** Resistivity, carrier concentration, and mobility of pure and doped  $\text{Cu}_2\text{O}$  samples

Sample	Sheet resistance ( $\Omega/\square$ )	Resistivity ( $\Omega \text{ cm}$ )	Carrier concentration ( $\text{cm}^{-3}$ )	Mobility ( $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ )
$\text{Cu}_2\text{O}$	$R_{\text{sh}} = 1.20 \times 10^6$	$\rho = 6$	$5.4 \times 10^{16}$	19
$\text{Cu}_2\text{O:H}$	$R_{\text{sh}} = 1.05 \times 10^6$	$\rho = 3.4$	$1.2 \times 10^{17}$	15
$\text{Cu}_2\text{O:N}$	$R_{\text{sh}} = 8.30 \times 10^4$	$\rho = 0.41$	$2.7 \times 10^{18}$	5.6
$\text{Cu}_2\text{O:N/H}$	$R_{\text{sh}} = 3.25 \times 10^4$	$\rho = 0.16$	$1.2 \times 10^{19}$	3.2

**Table 2** Cu/N atomic ratios measured by EDS in four different sets of N and N/H doped  $\text{Cu}_2\text{O}$  samples

	Set 1	Set 2	Set 3	Set 4
$\text{Cu}_2\text{O:N}$	Cu/N = 10.23	Cu/N = 9.19	Cu/N = 11.5	Cu/N = 9.24
$\text{Cu}_2\text{O:N/H}$	Cu/N = 10.33	Cu/N = 9.84	Cu/N = 12.62	Cu/N = 8.12

grown in the same conditions. These results derive from EDS analyses performed on different micro-areas of each sample. The average Cu/N atomic ratio is about 10 in N- and N/H-doped  $\text{Cu}_2\text{O}$  films. Considering that  $1 \text{ cm}^3$  of  $\text{Cu}_2\text{O}$  contains  $5.22 \times 10^{22}$  Cu atoms, such a Cu/N atomic ratio corresponds to a  $\text{N}_2$  concentration of  $2.6 \times 10^{21} \text{ cm}^{-3}$  when nitrogen enters the  $\text{Cu}_2\text{O}$  lattice as  $\text{N}_2$ . This value well agrees with the results of SIMS measurements of N doped  $\text{Cu}_2\text{O}$  films grown by RF sputtering with a high N content in the process gas.<sup>30</sup>

The optical properties were investigated by measuring the transmittance ( $T$ ) in UV-Vis-NIR range, between 280 and 1100 nm. In Fig. 1, the transmittance against the photon wavelength,  $\lambda$ , (and the photon energy,  $E$ ) and the square of the product of absorption coefficient and photon energy against the photon energy,  $E$ , are plotted in figures (A) and (B), respectively. The most relevant feature of the  $T$  spectra in Fig. 1(A) is the macroscopic difference between the  $\text{Cu}_2\text{O}$  and the  $\text{Cu}_2\text{O:H}$  spectra. This result clearly indicates that hydrogen strongly perturbs the defect electronic levels in the energy gap. In detail, in the  $\text{Cu}_2\text{O}$  spectrum the  $T$  values decrease from a maximum occurring for an  $E$  value around 2.3 eV towards an almost asymptotic value. The  $\text{Cu}_2\text{O}$  energy gap is estimated equal to 2.55 eV (see below). Thus, there are defect levels absorbing light in the 2.3–2.5 eV  $E$  range, possibly  $V_{\text{Cu}}$  vacancies that induce acceptor levels about 0.2 eV above VBM. For decreasing  $E$  values, the observed  $T$  lowering is induced by deep defects levels involved in the light absorption. Differently from  $\text{Cu}_2\text{O}$ , the  $\text{Cu}_2\text{O:H}$  spectrum does not show a maximum  $T$  value. A steep  $T$  rise in the 3.5–2.5 eV  $E$  range is followed by a monotonic  $T$  increase for decreasing  $E$  values. These results show that both the  $V_{\text{Cu}}$  acceptor levels and the deep defect levels occurring in the  $\text{Cu}_2\text{O}$  energy gap have been neutralized by the hydrogen introduction. This agrees with the above-mentioned results indicating that H behaves as an amphoteric impurity able to compensate/neutralize both acceptors and donors. Finally, they should be noted the similarities between the  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{O:N}$  spectra on one side and between the  $\text{Cu}_2\text{O:H}$  and  $\text{Cu}_2\text{O:N/H}$  spectra on the other side, which further confirm the relevant role of hydrogen on the transmittance evolution in the here investigated samples.

In Fig. 1(B), the optical band gap ( $E_g$ ) of the  $\text{Cu}_2\text{O}$  thin films was estimated based on the Tauc relation for allowed direct transitions  $(\alpha h\nu)^2 = A(h\nu - E_g)$  where  $A$  is a constant,  $h\nu$  is the photon energy,  $E_g$  is the allowed energy gap, and the absorption coefficient ( $\alpha$ ) is calculated from  $\alpha = -(\log T)/d$ , where  $d$  is the film thickness. The values for the optical band gaps, estimated by extrapolating the linear portion of the Tauc plots to the energy axis intercept, are 2.52 eV for  $\text{Cu}_2\text{O:N}$  and  $\text{Cu}_2\text{O:N/H}$ , 2.55 eV for  $\text{Cu}_2\text{O}$ , and 2.60 eV for the  $\text{Cu}_2\text{O:H}$  sample. Such



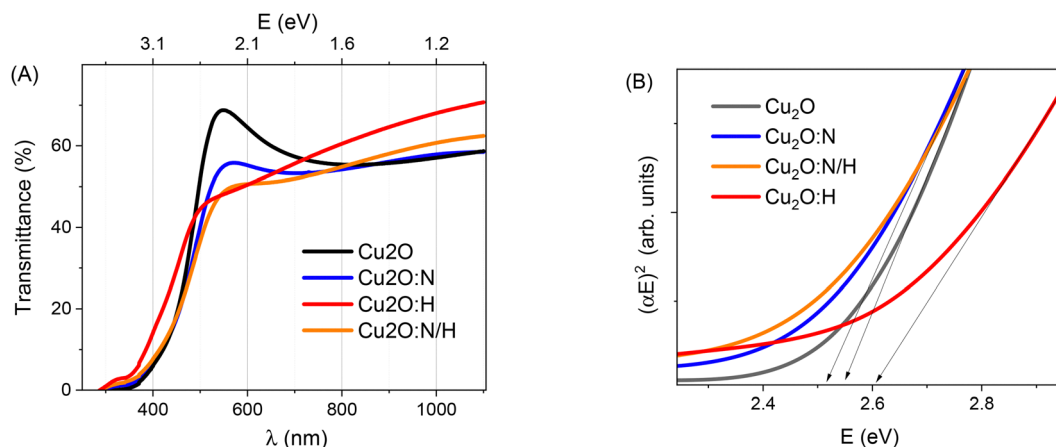


Fig. 1 (A) UV-vis-NIR transmittance spectra against the photon wavelength,  $\lambda$  (and the photon energy,  $E$ ), and (B) Tauc plot against the photon energy,  $E$ , of pure and doped  $\text{Cu}_2\text{O}$  films. The arrows indicate the estimated optical band gaps (the band gap values are basically identical for the  $\text{Cu}_2\text{O}$ :N and  $\text{Cu}_2\text{O}$ :N/H samples).

values are consistent with many reported results<sup>31–33</sup> and with the above discussed H effects.

### 3b. Structural characterization

XRD spectra were collected to exclude the presence of secondary phases possibly forming during the growth, since  $\text{Cu}_2\text{O}$  is not the thermodynamically most stable phase in the Cu–O binary phase diagram. The experimental diffraction patterns are reported in Fig. 2, while a comparative analysis is summarized in Table 3. Error bars are omitted in the table for clarity and are discussed in the main text. All of the films deposited in Ar, Ar +  $\text{H}_2$ , Ar +  $\text{N}_2$ , and Ar +  $\text{N}_2$  +  $\text{H}_2$  atmospheres exhibit the cubic  $\text{Cu}_2\text{O}$  phase (ICSD Card No. 031057) as the dominant crystalline component, identified by the characteristic (111) and (020) reflections. In all samples, the most intense peak corresponds to the  $\text{Cu}_2\text{O}$  (111) reflection (relative intensity of 100%). For films deposited in Ar ( $\text{Cu}_2\text{O}$ ), Ar +  $\text{H}_2$  ( $\text{Cu}_2\text{O}$ :H), and

Ar +  $\text{N}_2$  ( $\text{Cu}_2\text{O}$ :N), the (111) peak is located at  $36.41^\circ$ , while a slight shift to a lower angle ( $36.29^\circ$ ) is observed for the film grown in Ar +  $\text{N}_2$  +  $\text{H}_2$  ( $\text{Cu}_2\text{O}$ :N/H), corresponding to a relative variation of  $\sim 0.3\%$ . This shift suggests a small increase of the interplanar spacing from  $2.469 \pm 0.001 \text{ \AA}$  to  $2.471 \pm 0.001 \text{ \AA}$ , corresponding to a relative lattice distortion of  $\sim 0.08\%$  along the  $\langle 111 \rangle$  direction and to a derived lattice parameter variation from  $4.272 \pm 0.001 \text{ \AA}$  to  $4.281 \pm 0.002 \text{ \AA}$ . A similar, but weaker, trend is observed for the (020) reflection. The peak position shifts from  $42.08^\circ$  in  $\text{Cu}_2\text{O}$ , corresponding to an interplanar spacing of  $d(020) = 2.147 \pm 0.001 \text{ \AA}$ , to  $41.99^\circ$  and  $41.97^\circ$  in  $\text{Cu}_2\text{O}$ :N/H and  $\text{Cu}_2\text{O}$ :N, corresponding to  $d(020) = 2.151 \pm 0.001 \text{ \AA}$  and  $2.152 \pm 0.001 \text{ \AA}$ , respectively. These shifts correspond to a relative increase in the  $d$ -spacing of approximately 0.2%, indicating minor lattice distortions in samples  $\text{Cu}_2\text{O}$ :N/H and  $\text{Cu}_2\text{O}$ :N. A more pronounced shift is observed for the secondary (020) reflection in the  $\text{Cu}_2\text{O}$ :H sample. In this case, the peak position changes from  $42.08^\circ$  in the  $\text{Cu}_2\text{O}$  reference sample, corresponding to an interplanar spacing of  $d(020) = 2.147 \pm 0.001 \text{ \AA}$  and to a derived lattice parameter  $a = 4.294 \pm 0.002 \text{ \AA}$ , to  $41.28^\circ$  in  $\text{Cu}_2\text{O}$ :H sample, corresponding to  $d(020) = 2.188 \pm 0.001 \text{ \AA}$  and to a derived lattice parameter  $a = 4.376 \pm 0.002 \text{ \AA}$ . Such an appreciable angular shift of  $0.80^\circ$  corresponds to an increase in the interplanar spacing of  $\Delta d \approx 0.041 \text{ \AA}$ , corresponding to a relative variation of approximately 1.9%, and to a corresponding lattice parameter expansion along the (020) direction. Such a significant and anisotropic lattice expansion likely indicates a structural modification induced by hydrogen incorporation in the  $\text{Cu}_2\text{O}$ :H film. In addition to the peak position shift, the  $\text{Cu}_2\text{O}$ :H sample exhibits the lowest relative intensity of the (020) reflection within the series: the (020) peak reaches only 19% of the (111) intensity, compared to 42%, 49%, and 73% for samples  $\text{Cu}_2\text{O}$ ,  $\text{Cu}_2\text{O}$ :N, and  $\text{Cu}_2\text{O}$ :N/H, respectively. This strong suppression of the (020) intensity can be interpreted as a combined effect of preferred orientation and microstructural factors.  $\text{Cu}_2\text{O}$  thin-film studies have shown that changes in deposition conditions and post-treatments can significantly modify grain

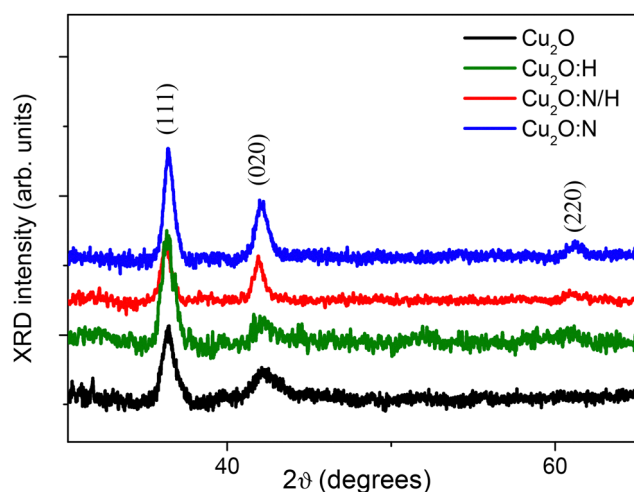


Fig. 2 XRD Diffractograms of  $\text{Cu}_2\text{O}$  films. Miller indexes correspond to the cubic  $\text{Cu}_2\text{O}$  phase.



Table 3 Comparative XRD analysis of pure and doped Cu<sub>2</sub>O samples

Peak Position (°)	Index(s)	Element	Intensity	Relative Intensity (%)	System	FWHM (°)	Crystallite Size (nm)	Card no.	Ref.
Sample ID	Cu <sub>2</sub> O								
36.41	(111)	Cu <sub>2</sub> O	1275	100	Cubic	0.76	11.6	031057	ICSD CC
42.08	(020)	Cu <sub>2</sub> O	534	42	Cubic	1.05	8.3	031057	ICSD CC
Sample ID	Cu <sub>2</sub> O:N/H								
36.29	(111)	Cu <sub>2</sub> O	1580	100	Cubic	0.56	15.6	031057	ICSD CC
41.99	(020)	Cu <sub>2</sub> O	1159	73	Cubic	0.54	16.5	031057	ICSD CC
Sample ID	Cu <sub>2</sub> O:N								
36.41	(111)	Cu <sub>2</sub> O	3762	100	Cubic	0.61	14.2	031057	ICSD CC
41.97	(020)	Cu <sub>2</sub> O	1849	49	Cubic	0.77	11.6	031057	ICSD CC
Sample ID	Cu <sub>2</sub> O:H								
36.40	(111)	Cu <sub>2</sub> O	1486	100	Cubic	0.76	11.0	031057	ICSD CC
41.28	(020)	Cu <sub>2</sub> O	279	19	Cubic	1.19	7.4	031057	ICSD CC

morphology and texture, leading to systematic variations in the  $I(111)/I(200)$  (or  $I(111)/I(020)$ ) ratio, which correlate with grain size, strain, and defect distribution in different crystallographic directions.<sup>34,35</sup> In sample Cu<sub>2</sub>O:H, the (020) reflection not only shifts but also displays the largest FWHM (1.19°) and the smallest crystallite size (7.4 nm) among the examined films, indicating a reduced coherent scattering domain and enhanced microstrain along this orientation. Such a microstructural disorder induces peak broadening and intensity attenuation, providing a possible explanation for the low (020) relative intensity compared to the stronger (111) reflection. Nevertheless, the diffraction pattern of sample Cu<sub>2</sub>O:H remains fully consistent with a single cubic Cu<sub>2</sub>O phase, and no additional reflections attributable to CuO or metallic Cu are detected. Regarding the crystallite size, sample Cu<sub>2</sub>O:N/H possesses the largest crystallites, samples Cu<sub>2</sub>O and Cu<sub>2</sub>O:H show the smallest crystallites, while sample Cu<sub>2</sub>O:N exhibits an intermediate size. No diffraction signatures corresponding to metallic copper (Cu) or copper oxide (CuO) phases are detected in all of the samples, confirming phase purity. In summary, XRD results indicate that the inclusion of hydrogen in the Cu<sub>2</sub>O films induces appreciable

structural changes which are substantially mitigated in films deposited in presence of hydrogen and nitrogen.

Micro-Raman measurements exploring the low and the high wavenumber regions (0–1000 cm<sup>-1</sup> and 2000–2500 cm<sup>-1</sup> respectively) are reported in Fig. 3. Such spectra show features which provide further information on the lattice quality and defect structure. The substrate was also measured and the so obtained Raman spectra (purple line) is also reported in Fig. 3 to rule out the glass contribution. In perfectly stoichiometric Cu<sub>2</sub>O (cuprite), the Raman spectrum is dominated by a single weak first-order F<sub>2g</sub> mode near ~109 cm<sup>-1</sup>. However, when structural disorder or point defects are present, otherwise silent infrared modes become Raman-active, giving rise to characteristic defect-related peaks. In defective Cu<sub>2</sub>O, the most frequently observed defect-activated bands are the T<sub>1u</sub> modes near ~148 cm<sup>-1</sup> and ~624–649 cm<sup>-1</sup>, and the second-order overtone of the silent 2E<sub>u</sub> mode around ~235 cm<sup>-1</sup>. These features are widely accepted as fingerprints of the Cu vacancy in the split configuration, V<sub>Cu,split</sub>, whereas the Cu vacancy, V<sub>Cu</sub>, does not induce appreciable signals.<sup>36</sup> The V<sub>Cu,split</sub> peak intensity scales with the defect concentration. In all of the present

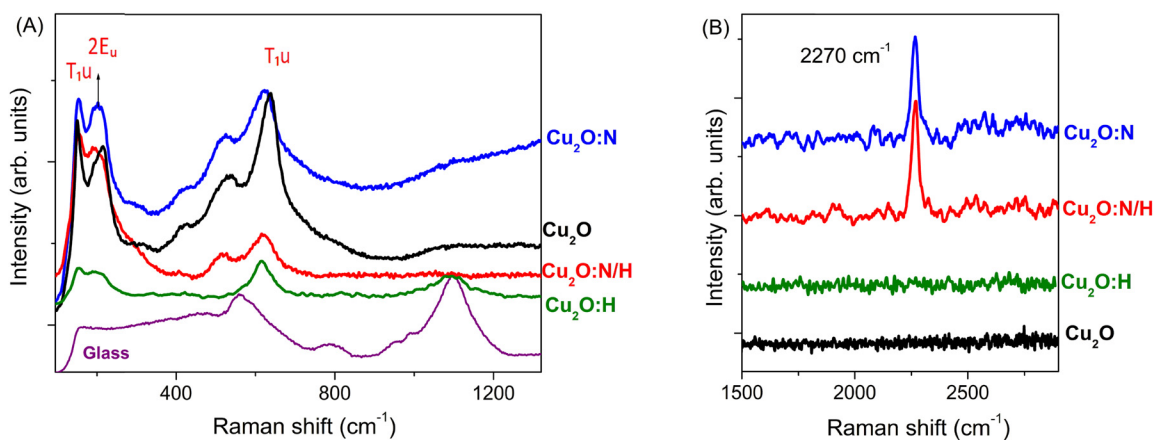


Fig. 3 Micro Raman patterns of Cu<sub>2</sub>O films and glass substrate collected in the low (A) and high (B) wavenumber regions.



samples, the spectra display bands at  $\sim 153\text{ cm}^{-1}$ ,  $\sim 210\text{ cm}^{-1}$  and  $\sim 620\text{--}640\text{ cm}^{-1}$ , as clearly visible in Fig. 3(A). The  $\sim 153\text{ cm}^{-1}$  feature is assigned to a defect-activated  $T_{1u}$  mode. This peak maintains its position in all of the present samples. The  $\sim 210\text{ cm}^{-1}$  band is attributed to the second-order  $2E_u$  overtone. It appears slightly upshifted to  $\sim 216\text{ cm}^{-1}$  (closer to the nominal position) in pristine  $\text{Cu}_2\text{O}$  in comparison with the samples  $\text{Cu}_2\text{O:N/H}$  and  $\text{Cu}_2\text{O:H}$ . A smaller shift is observed for the  $\text{Cu}_2\text{O:N}$  sample. A quite similar behavior is shown by the high-frequency line at  $\sim 620\text{ cm}^{-1}$ , which corresponds to a  $T_{1u}$  defect-activated mode. Thus, small shifts are observed only in H containing samples. More significant differences are found by comparing the peak intensities of the four sample spectra. First, by assuming  $\text{Cu}_2\text{O}$  as a reference sample, the intensities of all of the three peaks of the  $\text{Cu}_2\text{O:H}$  spectrum are dramatically reduced. This result indicates strong changes of the  $V_{\text{Cu,split}}$  local configuration induced by the presence of H. Second, still in comparison with  $\text{Cu}_2\text{O}$ , only the intensity of the line at  $\sim 620\text{ cm}^{-1}$  is strongly reduced in the  $\text{Cu}_2\text{O:N/H}$  sample. Finally, the intensities of the  $\sim 153\text{ cm}^{-1}$  and  $\sim 210\text{ cm}^{-1}$  bands show a slight increase in the  $\text{Cu}_2\text{O:N}$  spectrum, which appears, on the whole, very similar to the  $\text{Cu}_2\text{O}$  one. Thus, the presence of H appears to be a key factor to observe a strong or a noticeable perturbation of the  $V_{\text{Cu,split}}$  configuration.

Finally, as visible in Fig. 3(B), in the high-wavenumber region ( $2000\text{--}2500\text{ cm}^{-1}$ ), a distinct band is observed at  $\sim 2270\text{ cm}^{-1}$  in samples  $\text{Cu}_2\text{O:N}$  and  $\text{Cu}_2\text{O:N/H}$ , whereas for pristine  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{O:H}$  samples no measurable intensity above the noise level is detected in such region. We attribute the  $\sim 2270\text{ cm}^{-1}$  band to the local vibrational mode (LVM) of a defect-bound  $\text{N}_2$  dimer, specifically the  $\text{N}_2$  substituting on a Cu site ( $\text{N}_2$ )<sub>Cu</sub>, whose Raman-active stretching mode is expected around  $\sim 2280\text{ cm}^{-1}$  after non-harmonic correction (and clearly below the  $\sim 2330\text{ cm}^{-1}$  line of free molecular nitrogen). This assignment is consistent with first-principles calculations that predict: (i) ( $\text{N}_2$ )<sub>Cu</sub> to be a shallow acceptor, and (ii) an N-N LVM near  $2280\text{ cm}^{-1}$  for  $\text{N}_2$  on Cu sites, well separated from

both the free-molecule value and from the much lower frequencies predicted for  $\text{N}_2$  on O sites.<sup>21,22</sup> The absence of any peak near  $2330\text{ cm}^{-1}$  in all samples rules out a significant contribution from free or weakly physisorbed  $\text{N}_2$ , and supports the interpretation that the signal in  $\text{Cu}_2\text{O:N}$  and  $\text{Cu}_2\text{O:N/H}$  originates from  $\text{N}_2$  incorporated as a lattice defect rather than from ambient nitrogen.

### 3c. UPS measurements and electronic structure

UPS spectra of pure and doped  $\text{Cu}_2\text{O}$ , reported in Fig. 4(A), have been measured to explore the relative positions of the Fermi level,  $E_F$ , and the valence band maximum, VBM. Such positions have been obtained by linearly extrapolating the leading edge of the spectrum to the baseline. The VBM distance from  $E_F$  is  $0.5\text{ eV}$  in pure  $\text{Cu}_2\text{O}$ . Then, a shift of the VBM toward the  $E_F$  is observed and the  $E_F$ -VBM distance decreases progressively to  $0.35\text{ eV}$ ,  $0.25\text{ eV}$ , and  $0.15\text{ eV}$ , for the  $\text{Cu}_2\text{O:H}$ ,  $\text{Cu}_2\text{O:N}$ , and  $\text{Cu}_2\text{O:N/H}$  samples, respectively. This corresponds to a lowering of the Fermi level towards the VBM, as schematically reported in Fig. 4(B) for each sample. In the figure, the conduction band minimum (CBm) position is set to the mean of the bandgap values estimated from the Tauc plot of Fig. 1(B). A shift of the VBM with respect to the Fermi level was also shown by UPS spectra of N doped  $\text{Cu}_2\text{O}$  obtained by  $\text{N}^+$  implantation.<sup>23</sup> In that case, by comparison with pristine  $\text{Cu}_2\text{O}$ , a lowering of the Fermi level of  $0.35\text{ eV}$  was observed together with a significant reduction of the electrical resistance. In the present study, the  $E_F$  descent toward VBM shown in Fig. 4(B) can be accounted for by the appearance of acceptor states near the VBM. In fact, the results of the Hall measurements show a corresponding, progressive increase of the hole concentrations, see Table 1. The observed  $E_F$  evolution is also fully consistent with the results of resistivity measurements. In fact, the resistive value of  $\rho = 6\ \Omega\text{ cm}$  measured in pristine  $\text{Cu}_2\text{O}$  is in line with the position of  $E_F$  at  $0.5\text{ eV}$  from VBM. Then, the lowering of  $\rho$  to  $3.4\ \Omega\text{ cm}$ ,  $0.41\ \Omega\text{ cm}$ , and  $0.16\ \Omega\text{ cm}$  in the samples  $\text{Cu}_2\text{O:H}$ ,  $\text{Cu}_2\text{O:N}$ , and  $\text{Cu}_2\text{O:N/H}$ , respectively, is consistent with the

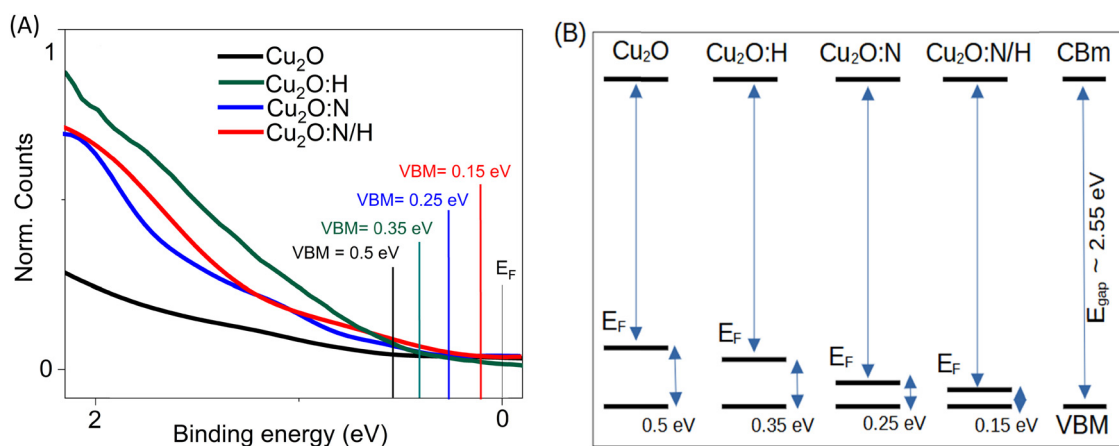


Fig. 4 (A) UPS spectra of pure, H doped, N doped, and N/H-doped  $\text{Cu}_2\text{O}$  thin films. The VBM position is estimated with respect to the Fermi level,  $E_F$ . (B) Representative scheme of the Fermi level positions with respect to the VBM. The CBm is set from the bandgap value derived from the Tauc plot of Fig. 1(B).



trend shown by the  $E_F$  positions at 0.35 eV, 0.25 eV, and 0.15 eV from VBM, respectively.

### 3d. Interpretative picture of present results

As illustrated in the previous sections, in the present study, the electrical and structural properties of a pristine  $\text{Cu}_2\text{O}$  sample have been investigated firstly by performing resistivity, Hall effect, XRD, UPS, and Raman measurements. Then, by using this  $\text{Cu}_2\text{O}$  sample as a reference, it has been considered how these same properties are affected by the introduction of H and N, individually, as well as by the simultaneous presence of both dopants. This systematic approach permits to perform a comparative analysis of the achieved results and data from the literature and, then, to draw an interpretative picture explaining the role of native defects and dopants in the evolution of the  $\text{Cu}_2\text{O}$  properties, in particular, in the achievement of a significant resistivity decrease. Such a comparative analysis will be performed here by considering results and data reported in a synoptic Table, see Table 4, to be used as a guide. For the sake of clearness, some of the above-discussed results will be briefly recalled in the following paragraphs.

As a preliminary note, different theoretical studies investigated the properties of native defects in  $\text{Cu}_2\text{O}$  as well as their interaction with H and N dopants. Among them, three recent studies have been selected here, since they use the most accurate, available theoretical methods for the investigation of semiconductor electronic properties and provide results in a good agreement with experimental findings.<sup>12,21,29</sup>

Concerning the pristine  $\text{Cu}_2\text{O}$  properties, one of the mentioned theoretical studies indicates the  $V_{\text{Cu}}$  and  $V_{\text{Cu,split}}$  vacancies as the most likely native defects.<sup>12</sup> These two Cu vacancies induce electronic levels in the energy gap 0.23 eV and 0.47 eV above VBM, respectively. These theoretical results are fully supported by experimental findings, see Table 4. Basing on such results, the weak p-type character of the present  $\text{Cu}_2\text{O}$  sample, indicated by a Fermi energy measured at 0.5 eV above VBM, a hole concentration of  $5.4 \times 10^{16} \text{ cm}^{-3}$ , and a corresponding, moderate resistivity of  $6.0 \Omega \text{ cm}$  can be accounted for by the quasi-shallow electronic level induced by  $V_{\text{Cu}}$ 's. Regarding the  $V_{\text{Cu,split}}$  vacancies, the presence of these defects in our sample is proved by the  $\text{Cu}_2\text{O}$  Raman spectrum showing the features generally considered as fingerprints of these defects, see Table 4.

Regarding the effects of H doping on the  $\text{Cu}_2\text{O}$  properties, as discussed in a previous section, a theoretical study<sup>29</sup> supported by the experiments<sup>10</sup> showed that the interaction of atomic H with  $V_{\text{Cu}}$  leads to the formation of  $V_{\text{Cu}}\text{-H}$  complexes. These complexes are ultra-deep defects inducing an electronic level at  $\sim 1.3$  eV above VBM, significantly higher than the quasi-shallow and the deep levels induced by  $V_{\text{Cu}}$  and  $V_{\text{Cu,split}}$ , respectively. Thus, H is expected to fully passivate the acceptor  $V_{\text{Cu}}$ 's. Here, present results show that in the  $\text{Cu}_2\text{O}:\text{H}$  sample a macroscopic change of the Raman spectrum occurs with respect to the  $\text{Cu}_2\text{O}$  spectrum. All of the vibrational line intensities attributed to the  $V_{\text{Cu,split}}$  vacancies significantly decrease, see Table 4, thus indicating a noticeable change of the local  $V_{\text{Cu,split}}$  configuration. It should be noted that this  $V_{\text{Cu,split}}$  evolution parallels the noteworthy lattice variation revealed by the comparison of the  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{O}:\text{H}$  XRD results discussed above. Such a major change of the  $V_{\text{Cu,split}}$  configuration cannot be induced by the scarcely reactive hydrogen molecule. Instead, it can be reasonably assumed that the peculiarities of the here used growth procedure (the Ar atoms and the  $\text{H}_2$  molecules undergo an electrical discharge and acquire an increasing kinetic energy before reaching the target) favor the introduction of the more reactive, atomic H in the  $\text{Cu}_2\text{O}$  sample. In presence of H atoms, the formation of  $V_{\text{Cu}}\text{-H}$  complexes and the ensuing  $V_{\text{Cu}}$  passivation can be safely supposed. On the other hand, although the effects of atomic H interaction with  $V_{\text{Cu,split}}$  vacancies are unknown, the strong change of the  $V_{\text{Cu,split}}$  configuration indicated by the Raman results makes highly probable the formation of some kind of  $V_{\text{Cu}}\text{-H}$  complexes, possibly accompanied by a  $V_{\text{Cu,split}}$  evolution from a deep to an ultra-deep acceptor defect. Anyway, on the whole, the H introduction should induce a reduction of the sample p-type character. Surprisingly, the results achieved for the  $\text{Cu}_2\text{O}:\text{H}$  sample show instead an appreciable decrease of the Fermi level distance from VBM, a small decrease of the resistivity value and, most important, an increase of the hole concentration, see Table 4. These unexpected results represent an important indication since they show that H can enhance the  $\text{Cu}_2\text{O}$  p-type character despite its ability to passivate the acceptor  $V_{\text{Cu}}$ 's initially responsible of such a character. These results are further surprising because the above-mentioned theoretical study<sup>29</sup> excludes the appearance of new, shallow acceptor defects induced by some H effect. Moreover, the same study and the results of the experimental studies discussed

**Table 4** Synoptic table reporting present values of resistivity,  $\rho$ , Fermi energy position with respect to the valence band maximum (VBM),  $E_F$ , hole concentrations, experimental and theoretical estimates of the positions of defect electronic levels with respect to VBM taken from the literature, positions of Raman lines in spectra measured in the present work (p.w.) and taken from literature (liter.). In the table, the arrows  $\downarrow$  indicate a significant decrease of the Raman line intensity

Sample	$\rho$ ( $\Omega \text{ cm}$ )	$E_F$ (eV)	Hole conc. ( $\text{cm}^{-3}$ )	Electr. lev. eV (exp) <sup>10</sup>	Electr. lev. eV (theor.) <sup>12,21,29</sup>	Raman $\text{cm}^{-1}$ (p.w.)	Raman $\text{cm}^{-1}$ (liter.)
$\text{Cu}_2\text{O}$	6.00	0.50	$5.4 \times 10^{16}$	0.22 ( $V_{\text{Cu}}$ ), $\sim 0.4$ ( $V_{\text{Cu}}\text{-s}$ )	0.23 ( $V_{\text{Cu}}$ ), 0.47 ( $V_{\text{Cu}}\text{-s}$ ) <sup>12</sup>	153, 210, 620–640	148, 235, 624–649
$\text{Cu}_2\text{O}:\text{H}$	5.00	0.35	$1.2 \times 10^{17}$	$\sim 1.3$ ( $V_{\text{Cu}}\text{-H}$ )	1.15 ( $V_{\text{Cu}}\text{-H}$ ) <sup>29</sup>	153 ( $\downarrow$ ), 210 ( $\downarrow$ ), 620–640 ( $\downarrow$ )	
$\text{Cu}_2\text{O}:\text{N}$	0.41	0.25	$2.7 \times 10^{18}$	0.16 ( $\text{N}_2$ ) <sub>Cu</sub>	0.20 ( $\text{N}_2$ ) <sub>Cu</sub> <sup>21</sup>	153, 210, 620–640, 2270	2280
$\text{Cu}_2\text{O}:\text{N}/\text{H}$	0.16	0.15	$1.2 \times 10^{19}$	0.16 ( $\text{N}_2$ ) <sub>Cu</sub> , $\sim 1.3$ ( $V_{\text{Cu}}\text{-H}$ )	0.20 ( $\text{N}_2$ ) <sub>Cu</sub> <sup>21</sup> , 1.15 ( $V_{\text{Cu}}\text{-H}$ ) <sup>29</sup>	153, 210, 620–640 ( $\downarrow$ ), 2270	2280



above<sup>24–28</sup> indicate that H behaves as a deep amphoteric impurity in Cu<sub>2</sub>O, able to compensate/neutralize both acceptors and donors. Thus, the only reasonable explanation of the here observed Fermi level descent and hole concentration increase is that H mainly compensates/passivates native donor defects, thus inducing an increase of the acceptor concentration. This result can be related to the findings of the above-mentioned study where H was introduced during the Cu<sub>2</sub>O growth and high temperatures favored the occurrence of quite large grains.<sup>24</sup> An increase of the Hall mobility was observed in that study, together with minor changes of the hole concentration. Those results were accounted for by showing that H accumulated at the grain boundaries, where it neutralized donor defects with minor effects on the inner-grain acceptor defects. An investigation of the H effects on the grain boundary defects is beyond the scope of the present work. However, it can be noted that even in the present study H is introduced during the Cu<sub>2</sub>O growth, but, the here used room temperature conditions induce the formation of much smaller grains (see Table 3). This results in a higher, overall surface/volume ratio. Thus, it can be suggested that, similarly to the mentioned study, H accumulated at the grain boundaries neutralizes donor defects to a greater extent than inner-grain acceptors and this effect is amplified by the larger exposed surface, thus accounting for an overall increase of the acceptor number.

About nitrogen doping, a recent theoretical study investigated different interstitial and substitutional sites for N atoms and N<sub>2</sub> molecules introduced in the Cu<sub>2</sub>O lattice and showed that a N atom substituting an oxygen atom (N<sub>O</sub>) and a nitrogen molecule occupying the V<sub>Cu</sub> site, (N<sub>2</sub>)<sub>Cu</sub>, are the lowest energy defects.<sup>21</sup> The latter defect becomes the favorite one in Cu-poor growth conditions. Moreover, N<sub>O</sub> and (N<sub>2</sub>)<sub>Cu</sub> behave as a deep and a shallow acceptor, respectively. These results have been fully confirmed by a subsequent, experimental study which ruled out the formation of N<sub>O</sub> and supported that of (N<sub>2</sub>)<sub>Cu</sub> by confirming also the shallow acceptor character of the latter defect,<sup>10</sup> see the position of the corresponding defect electronic levels in Table 4. In the case of the present Cu<sub>2</sub>O:N sample, the corresponding Raman spectrum is very similar to the Cu<sub>2</sub>O one in the low-wavenumber region (0–1200 cm<sup>-1</sup> range), see Table 4, thus indicating that N introduced in the sample does not perturb the native V<sub>Cu,split</sub> vacancies. This indirectly indicates that N is mainly present in the sample in the molecular form, less reactive than the atomic form. The presence of N<sub>2</sub> molecules in our sample should favor the formation of (N<sub>2</sub>)<sub>Cu</sub> complexes. As a matter of fact, such an occurrence is confirmed by the Raman line measured in the Cu<sub>2</sub>O:N sample in the high-wavenumber region at 2270 cm<sup>-1</sup>, close to the value indicated by theory and experiment for the (N<sub>2</sub>)<sub>Cu</sub> complexes.<sup>10,21</sup> Due to their shallow acceptor character, the presence of (N<sub>2</sub>)<sub>Cu</sub> complexes in our sample perfectly accounts for the significant Fermi level descent toward the VBM, the significant increase of the hole concentration, as well as for the consistent, remarkable resistivity decrease, observed in the Cu<sub>2</sub>O:N sample in comparison with the Cu<sub>2</sub>O one, see Table 4.

Finally, a further Fermi level descent toward VBM and a parallel increase of the hole concentration and resistivity decrease characterize the simultaneous doping with N and H realized in the Cu<sub>2</sub>O:N/H sample in comparison with the Cu<sub>2</sub>O:N one. In the former sample, driven by the above results, we expect that N<sub>2</sub> molecules occupy the V<sub>Cu</sub> sites by forming (N<sub>2</sub>)<sub>Cu</sub> shallow acceptors. Moreover, by considering that the formation of V<sub>Cu</sub>-H complexes comes from the H interaction with the O dangling bonds facing the V<sub>Cu</sub> site and that, in the (N<sub>2</sub>)<sub>Cu</sub> complex, these dangling bonds are not available (since involved in the formation of O–N bonds), we expect that such a complex is not affected by the presence of H atoms. Actually, the occurrence of unperturbed (N<sub>2</sub>)<sub>Cu</sub> complexes in our sample is confirmed by the appearance of the above-mentioned line at 2270 cm<sup>-1</sup> also in the Cu<sub>2</sub>O:N/H Raman spectrum. As discussed above, instead, atomic H can strongly perturb the V<sub>Cu,split</sub> vacancies. These vacancies are not affected by the presence of N<sub>2</sub> molecules, as shown by the similarity of the low-wavenumber region Cu<sub>2</sub>O:N Raman spectrum with that of the pristine Cu<sub>2</sub>O, see Table 4. Thus, in principle, even in the Cu<sub>2</sub>O:N/H film, H should induce strong changes of the V<sub>Cu,split</sub> configuration as those indicated by the evolution of the Cu<sub>2</sub>O:H Raman spectrum, see Table 4. In a partial agreement with such an expectation, in comparison with the Cu<sub>2</sub>O and Cu<sub>2</sub>O:H Raman spectra, in the low-wavenumber region the Cu<sub>2</sub>O:N/H Raman spectrum shows a significant reduction of the peak intensity only in the case of the 620–640 cm<sup>-1</sup> line. This suggests the occurrence of an appreciable change of the local V<sub>Cu,split</sub> configuration induced by the interaction with H which seems to be, however, somewhat different from that occurring in the Cu<sub>2</sub>O:H sample. It should be noted, once again, that the occurrence of a V<sub>Cu,split</sub> configuration change in the Cu<sub>2</sub>O:N/H sample agrees with the small, but still appreciable, lattice variation observed in this sample with respect to pristine Cu<sub>2</sub>O, discussed above. Basing on all of the above results and considerations, in the case of the simultaneous N and H doping of Cu<sub>2</sub>O, we can draw the following conclusions: (i) N<sub>2</sub> molecules introduced in the Cu<sub>2</sub>O lattice occupy the V<sub>Cu</sub> sites by forming (N<sub>2</sub>)<sub>Cu</sub> shallow acceptors, (ii) hydrogen introduced in the atomic form during the growth procedure does not perturb the (N<sub>2</sub>)<sub>Cu</sub> complexes, (iii) H atoms induce some configuration change of the V<sub>Cu,split</sub> vacancies (which are not affected by the presence of N<sub>2</sub> molecules), and (iv) as discussed above, hydrogen mainly compensates/neutralizes native shallow donors, thus making active the (N<sub>2</sub>)<sub>Cu</sub> acceptors that are compensated in the Cu<sub>2</sub>O:N sample. This leads to an overall increase of shallow acceptors, thus accounting well for the further Fermi level descent, hole concentration increase, and resistivity decrease observed in the Cu<sub>2</sub>O:N/H sample with respect to the Cu<sub>2</sub>O:N one.

In conclusion, the above analysis shows that all of the present results can be collected in a coherent, qualitative picture which fully accounts for how an extra-low resistivity can be achieved in nitrogen and hydrogen doped Cu<sub>2</sub>O films.



## 4. Conclusions

In the present study, it is shown that Cu<sub>2</sub>O films with an extra-low resistivity can be grown by RF sputtering by exploiting nitrogen and hydrogen doping. Significantly, two peculiar features distinguish the present study from previous ones: the two dopants are simultaneously introduced in the Cu<sub>2</sub>O films during the growth and the growth process is performed at room temperature. The effects of N and H doping on the Cu<sub>2</sub>O properties have been investigated by performing resistivity, Hall effect, XRD, UPS and Raman measurements on four different kinds of samples: a pristine Cu<sub>2</sub>O film, Cu<sub>2</sub>O films doped with N and H individually, as well as a Cu<sub>2</sub>O film containing both dopants. Such a systematic investigation of the doping effects has permitted to perform a comparative analysis of the achieved results and data from literature and to draw a sound, consistent picture explaining the role of native defects and the N and H dopants in the successful achievement of extra-low resistivity values.

## Author contributions

ADT, ADC and AAB conceived the idea and planned the work. Film growth, PML, SA and ADT; XRD and Raman characterization, BP, AG; transmittance measurements, PML, SA; UPS characterization, AC, DB, and ML; writing – original draft preparation, ADT and AAB; and writing – review and editing, ADC, ADT, BP, AAB, FF. All authors discussed the results and commented on the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this study are available in the published article and at <https://zenodo.org>, DOI:<https://doi.org/10.5281/zenodo.18771428>.

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