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Electrical Properties and Behaviors of Cuprous Oxide Cubes under High Pressure

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S Supporting Information

ABSTRACT: An accurate in situ electrical resistivity measurement of cuprous oxide cubes has been conducted in a diamond anvil cell at room temperature with pressures up to 25 GPa. The abnormal electrical resistivity variation found at 0.7−2.2 GPa is attributed to the phase transformation from a cubic to a tetragonal structure. Three other discontinuous changes in the electrical resistivity are observed around 8.5, 10.3, and 21.6 GPa, corresponding to the phase transitions from tetragonal to pseudocubic to hexagonal to another hexagonal phase, respectively. The first-principles calculations illustrate that the electrical resistivity decrease of the tetragonal phase is not related to band-gap shrinkage but related to a higher quantity of electrons excited from strain-induced states increasing in band gap with increasing pressure. The results indicate that the Cu_2O cubes begin to crush at about 15 GPa and completely transform into nanocrystalline at 25 GPa.

Under ambient conditions, cuprous oxide (Cu_2O) has a typical p-type direct band gap (2.17 eV).[1] Because of its applications in solar energy conversion materials,[2] electrode materials,[3] sensors,[4] and catalysts,[5] Cu_2O has attracted much attention over the past decades. Under compression, Cu_2O is also a topic of interest for its unique properties, such as its structural transition behavior,[6−8] anomalous elastic behavior,[9] negative thermal expansion,[10] mechanical stability,[11] and electrical properties.[12] The structural behavior of Cu_2O has been studied by the X-ray diffraction (XRD) method;[6−8] however, the results showed obvious discrepancies in Cu_2O phase transitions.

In 1982, Werner and Hochheimer[6] stated that a series of phase transitions might occur in Cu_2O under high pressure: cubic phase (0−10 GPa) → hexagonal phase with unknown structural details (10−18 GPa) → hexagonal phase in $CdCl_2$-type structure (above 18 GPa). In 2003, Machon et al.[7] gave a more detailed analysis on the Cu_2O structure up to 11 GPa. They observed a phase transition from cubic to tetragonal structure in 0.7−2.2 GPa and another phase transition from tetragonal to pseudocubic at 8.5 GPa. In 2004, Sinitsyn et al.[8] conducted experiments up to 30 GPa and observed a phase transition from cubic to hexagonal at 11 GPa. However, they did not observe the $CdCl_2$-type structure above 18 GPa. Instead, they announced a hexagonal phase with a simple structure at about 21 GPa.

Obviously, the studies on the Cu_2O structure by XRD did not provide a uniform result. The issue concerning the existence of the tetragonal and pseudocubic phases below 11 GPa, the structural phase transition from 18 to 25 GPa, has remained controversial. Besides, the mechanical stability of the Cu_2O crystal under high pressure has been studied by Machon et al.,[7] Sinitsyn et al.,[8] and Ponyatovski et al.[13] A size reduction in Cu_2O crystals with increasing pressure has been observed, but the details of this pressure-induced crush remain unclear.

Generally, both structure transitions and crush of Cu_2O cubes can affect its electrical properties. High-pressure in situ electrical resistance measurement is a good tool to reflect the phase transition behavior. In 1989, Bourne et al.[12] demonstrated only one abrupt resistance change at 10 GPa corresponding to the phase transition from the cubic to hexagonal phase.[6,8] We attribute the reason why they did not observe other phase transitions to the low measurement accuracy of their experiment. In this paper, an accurate in situ electrical resistivity measurement under high pressure has been carried out to determine the electrical behavior of Cu_2O cubes during the phase transition (see the details in S1 in the Supporting Information). Meanwhile, to make clear the relationship between the electrical transportation properties and band-gap sizes of tetragonal Cu_2O, pressure-dependent band structure calculations were performed[14] (see the details in S2 in the Supporting Information).

The pressure-dependent electrical resistivity of Cu_2O cubes at room temperature is displayed in Figure 1. The resistivity decreases gradually with increasing pressure and reaches a minimum at about 0.7 GPa. From 0.7 to 2.2 GPa, the resistivity increases smoothly with increasing pressure and reaches a maximum at about 2.2 GPa. In this region (0.7−2.2 GPa), a phase transition from cubic to tetragonal had been determined by Machon and co-worker using XRD.[7] Therefore, we attribute the behavior of resistivity upon compression from 0.7 to 2.2 GPa to this phase transition. It should be noticed that the resistivity has a fast drop from ambient to 0.7 GPa. Two factors are related to this drop. As cubes were filled into the cell, a lot

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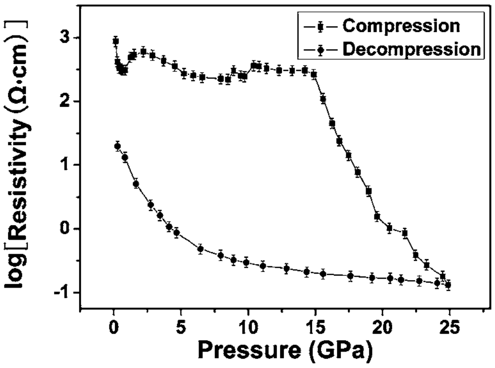

Figure 1. Pressure-dependent resistivity of Cu_2O cubes at room temperature. The error is less than 5%.[15] The solid squares and circles denote compression and decompression processes, respectively.

of gaps with big resistivity remained among cubes. With increasing pressure, the density of the gaps decreased quickly and caused a rapid decrease in resistivity. Meanwhile, pressure introduced a large number of strains[7] and a related strain-induced energy level in the energy gap, which led to a decrease in resistivity.

From 2.2 to 8.5 GPa, the resistivity drops again with increasing pressure. For a semiconductor, the compression can drive an atom to deviate from its equilibrium site and bring about additional strain-induced energy levels in the band gap. Under compression, electronic conduction of the semiconductor is dominated by electrons excited from the valence band to the conduction band, impurity level, or other levels in the gap such as the strain-induced level.[16] Both pressure-induced band-gap shrinkage and the strain-induced level can cause increasing conductivity. For further information about the resistivity decrease in tetragonal Cu_2O, pressure-dependent band-gap data were obtained by GGA-PBE approximations, as shown in Figure 2. All of the band gaps at 3, 4, 5, 6, 7, and 8 GPa in the figure are derived from the calculations. Two calculated band structures at 3 and 8 GPa are shown in the inset. The calculated results indicate that the tetragonal Cu_2O cube is a direct narrow-gap semiconductor.

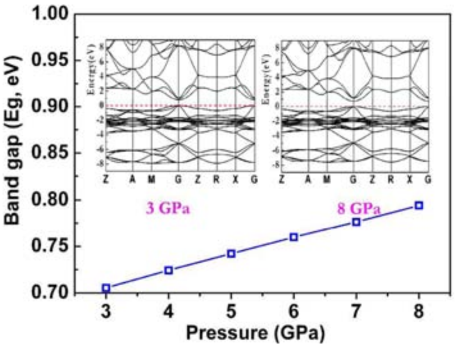

Figure 2. Pressure-dependent band-gap sizes (E_g in electronvolts) by GGA-PBE approximations. Inset from left to right: calculated electronic band structures of tetragonal Cu_2O at 3 and 8 GPa, respectively. The zero-energy lines indicate the top of the valence band.

From the Figure 2, it can be found that the gap width increases linearly with a velocity of 0.016 eV/GPa as the pressure is increased from 3 to 8 GPa. Because the band-gap increase was found for tetragonal Cu_2O, excitation of the localized electron states in the gap is associated with the strain-induced level. Pressure-induced ionization of impurity level is usually utilized to understand the effect of the pressure on the electrical properties of the semiconductor.[17] Around 8.5 GPa, an abrupt resistivity increase has been observed, which reflects the structural transition from a tetragonal to a pseudocubic phase.[7] A similar resistivity change has also been found around 10.3 GPa, which is related to the phase transition from the pseudocubic to hexagonal structure.[6,8,12] As the pressure is increased from 15 to 25 GPa, the resistivity drops in 3 orders of magnitude. A fluctuation in the resistivity has been observed at 21.6 GPa, which can be attributed to the phase transition reported by Sinitsyn et al.[8]

We noticed that these unusual changes in the resistivity at 0.7, 2.2, 8.5, and 21.6 GPa were not reported in ref 12, where Cu wires were used as electrical probes for resisitivity detection. The reason for this phenomenon may be related to the relative lower measurement accuracy compared to our work. In ref 8, the three most possible experimental conditions that may lead to these discrepancies as proposed by the authors are the hydrostaticity, the initial grain size, and the compression rate. All of these experimental conditions and results that may lead to discrepancies are listed in Table S3 (Supporting Information). By comparing the data in the table, we find both the different measurement accuracy and the initial grain size of the samples are the reason why our experiments yield results different from those in ref 12 (see the details in S3 in the Supporting Information.

Both the phase transitions and the crush of Cu_2O cubes can affect electron-transport capabilities. According to previous reports,[6−8] no phase transformation of Cu_2O occurs at 15 GPa, and the fast decrease in the resistivity after 15 GPa can be attributed to the pressure-induced crush of the Cu_2O cubes. Scanning electron microscopy (SEM) and high-resolution transmission electron microscope (HRTEM) were done after decompression to confirm this judgment.

The initial average grain size of the samples was measured as 800 nm.[18] The surface morphologies of the sample after decompression from 5, 10, 15, 20, and 25 GPa are shown in parts a−f in Figure 3, respectively. The pressure-induced crush of Cu_2O cubes can be observed around 15 GPa, as shown in Figure 3c. As the pressure reaches 20 GPa, the samples are no longer cubes, as shown in Figure 3d; there is a clear decrease in the grain size. As can be seen from Figure 3e, the crystals are compressed into a single compact unit after decompression from 25 GPa to ambient pressure.

HRTEM was used to detect the grain size of the samples after depression from 25 GPa. From Figure 3f, it can be found that the average particle size deceases to about 6 nm, and the crushed domains with arbitrary shapes retain their characteristics of single crystals. This result indicates that the pressure-induced crush of Cu_2O cubes yields abundant nanocrystals with random crystal direction, which makes numerous boundaries and microstrains in the sample. Both microstrains and grain boundaries can introduce additional energy levels in the band gap and then cause the concentration of the free charge carrier to increase. As a result, the electrical resistivity decreases above 15 GPa.

As the pressure was released to ambient conditions, the resistivity returned from the low-value state at 25 GPa to the high-value state, indicating that the pressure-induced phase transitions of Cu_2O are reversible. The same conclusions were also given in previous reports.[6,8,12] The resistivity difference

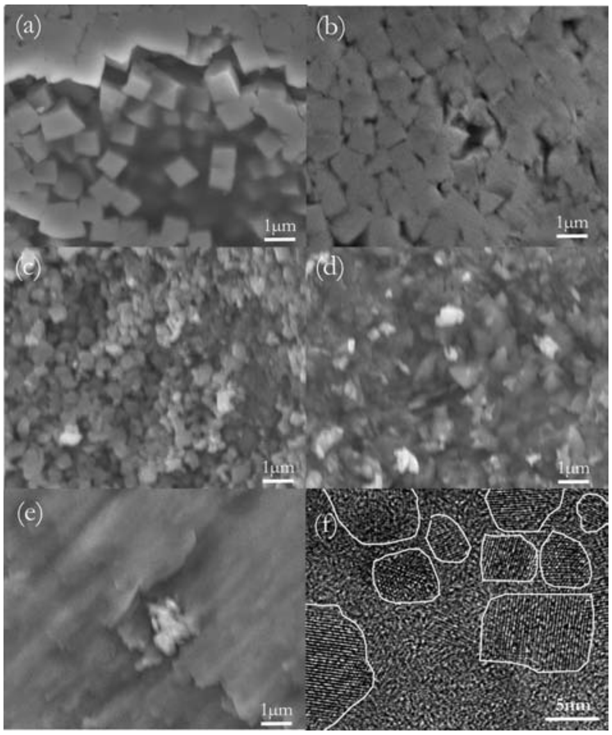

Figure 3. SEM images of the Cu_2O sample after decompression from different pressures: (a) 5 GPa; (b) 10 GPa; (c) 15 GPa; (d) 20 GPa; (e) 25 GPa; (f) HRTEM image of Cu_2O sample after decompression from 25 GPa. The white curves denote the boundary of the nanodomains.

between the original and final states is attributed to the pressure-induced cubes crushing and particle fining, which make the cubes become nanocrystals and bring numerous related energy levels in the gap. However, no abnormal change in the resistivity plot was found in the decompression process. This is due to two factors: (1) the hysteresis effect of the high-pressure phase of Cu_2O; (2) the abrupt change in the resistivity caused by the related phase transition being relatively small and emerging from the resistivity drop related to the cube crush.

In summary, with a specially designed DAC, the electrical resistivity of Cu_2O cubes has been studied by in situ electrical measurements under high pressure. HRTEM and SEM investigations and theoretical calculations have also been used in this study. The results demonstrate that the abrupt resistivity changes at 0.7−2.2, 8.5, 10.3, and 21.6 GPa can be attributed to the phase transitions mentioned in the earlier X-ray studies. Theoretical calculations show that the decrease of the electrical resistivity in tetragonal Cu_2O is mostly due to the increase of the strain-induced energy levels in the band gap with increasing pressure. HRTEM and SEM detection indicate that the decrease of the resistivity at pressures above 15 GPa is brought on by the crush of Cu_2O cubes. The particle sizes of the Cu_2O cubes change from 800 nm to about 6 nm after decompression from 25 GPa.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Comparison of our in situ high-pressure electrical measurement with ref 12 (S1) and details of the computational methods and all calculation parameters (S2) and analysis of the experimental conditions and results in refs 6−8 and 12 and our work (S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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