Supplementary information

Nearly Constant Electrical Resistance over Large Temperature Range in Cu_3NM_x (M = Cu, Ag, Au) Compounds

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Section I Supplementary Fig. S1-S5

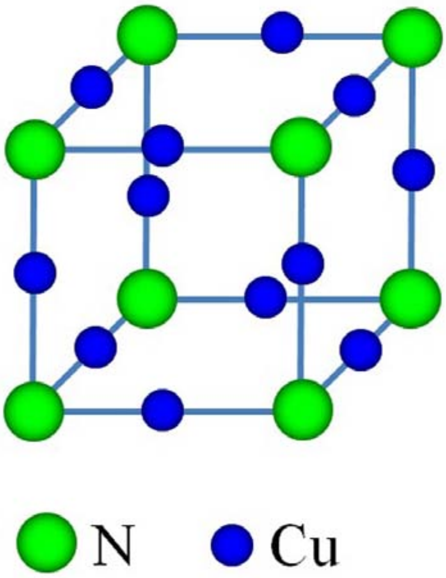

Fig. S1. Schematic sketch of the unit cell for Cu_3N. Lattice constant: a = 0.383 nm.

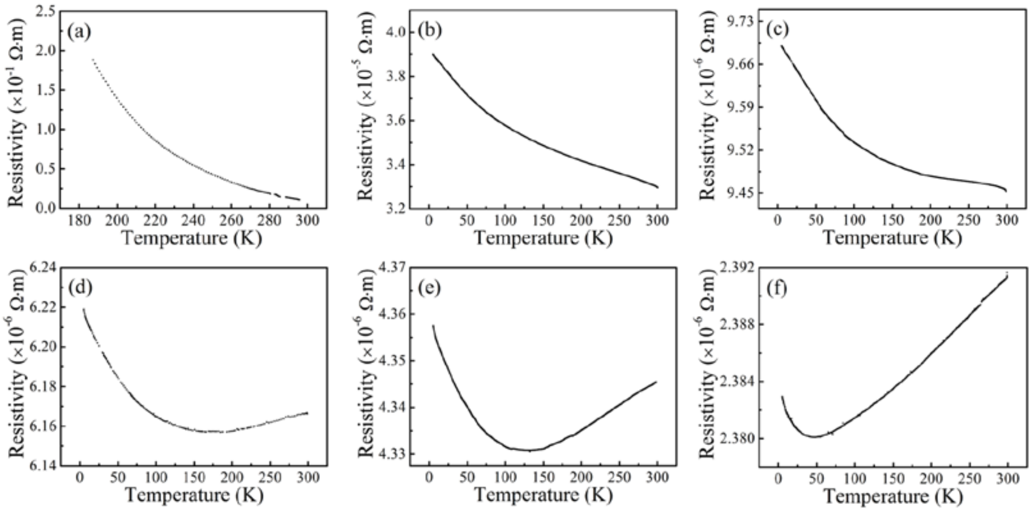

Fig. S2. Temperature dependence of electrical resistivity for Cu_3NCu_x for (a) x = 0.0; (b) x = 0.33; (c) x = 0.47; (d) x = 0.59; (e) x = 0.70; (f) x = 0.74.

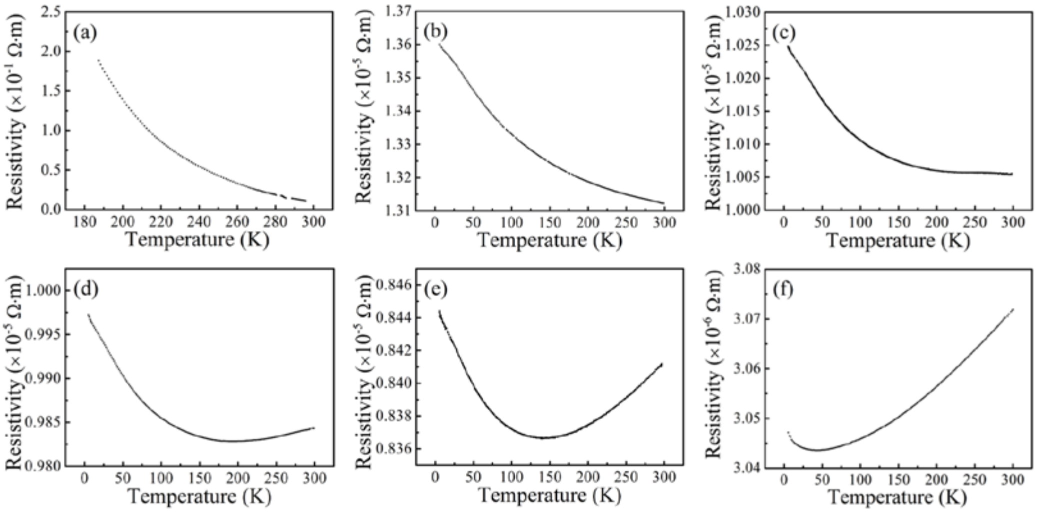

Fig. S3. Temperature dependence of electrical resistivity for Cu_3NAg_x for (a) x = 0.0; (b) x = 0.57; (c) x = 0.69; (d) x = 0.73; (e) x = 0.85; (f) x = 1.0.

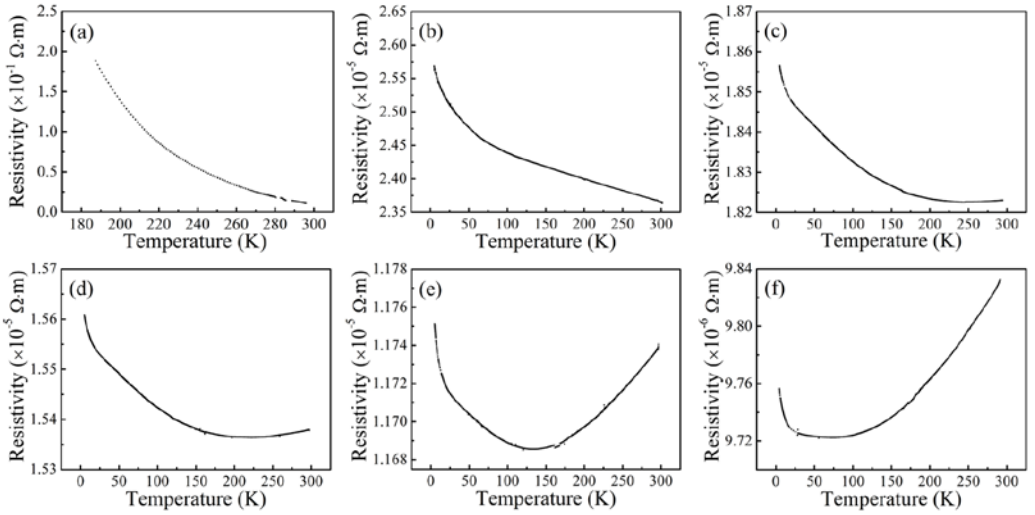

Fig. S4. Temperature dependence of electrical resistivity for Cu_3NAu_x for (a) x = 0.0; (b) x = 0.27; (c) x = 0.33; (d) x = 0.37; (e) x = 0.42; (f) x = 0.49.

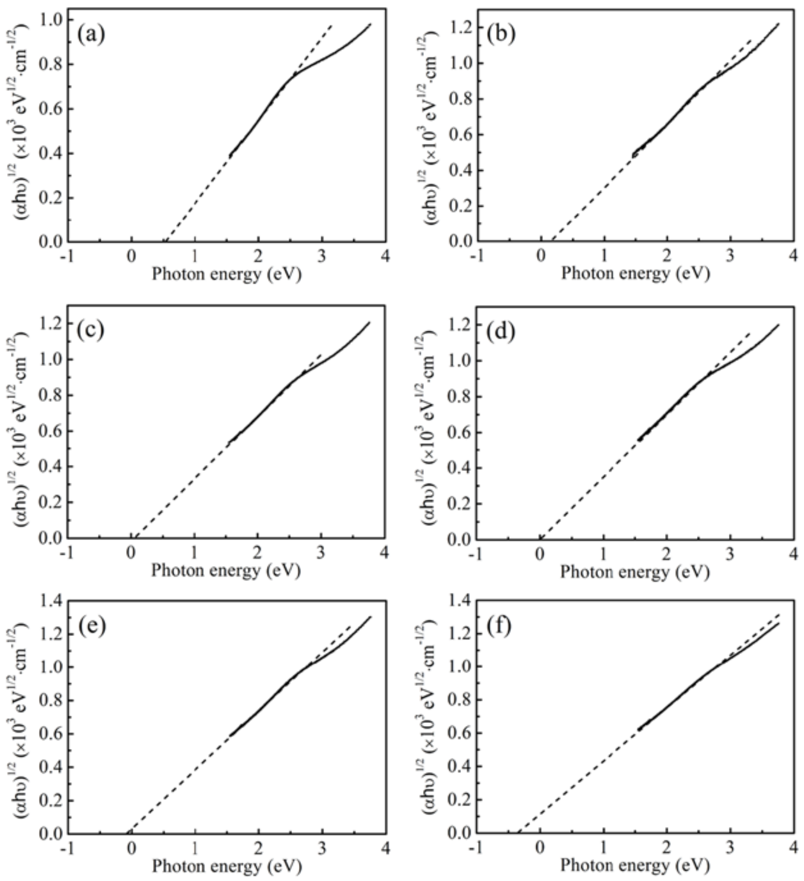

Fig. S5. The $(\alpha h\nu)^{1/2}$ vs. $h\nu$ curves drawn on the absorption spectral data for $\mathbf{Cu_3NAg_x}$ with (a) x = 0.0; (b) x = 0.57; (c) x = 0.69; (d) x = 0.73; (e) x = 0.85; (f) x = 1.0. For x varying from 0.0 to 0.73, the intercept of the fitting line with the abscissa moves steadily towards zero, indicating a vanishing band gap in the sample.

Section Ⅱ. Site occupation of impurity Ag and Au atoms in deposit

The determination of precise site occupation in a compound is a challenging and painstaking work. For crystalline samples of a high quality, many unique reflections are available on the XRD patterns. The patterns can be used for solution of the crystal structure. With further structure refinement, some conclusive claims about site occupation in the crystal can be obtained. Another technique, EXAFS, can resolve into individual site occupation preferences. The orientation dependence of characteristic X-ray emissions can also partially serve this purpose. The precise determination of the impurity Ag or Au atoms in the deposits is beyond the scope of the current work. Notice that even for the binary Cu_3N, the nearly stoichiometric samples are just nanocrystalline deposits with crystallites of a typical size of ~40 nm[1], which may not be a good choice for refined solution of crystal structure by XRD. Yet, we believe that the impurity Ag or Au atoms occupy most probably the center of the unit cells of the Cu_3N lattice:

(1) The relative stronger Cu-N bond is preferable. If the Ag or Au atoms occupied the edge centers instead of the body center of the unit cell, the lattice constant, i.e., the edge length, would be much larger, noticing that the lattice constant for Ag_3N in the same structure is as large as 0.4328 nm[2]. The substitution of Cu atoms by Ag or Au atoms in a Cu_3N lattice with cell centers occupied by extra metal atoms is even more unfavorable. This leads to the occurrence of Cu vacancies which provides a better explanation for lattice constant of deposits of higher doping level[3].

(2) Starting from the intrinsic Cu_3N sample, the structure of the deposits with incorporation of more Ag or Au atoms was monitored by XRD. For all the deposits, the characteristic (100)- and (200) reflections of the Cu_3N lattice are well preserved. Only very small change of lattice distortion was observed. In fact, all the lattice constants in Cu_3NAg_x ($x \leq 0.85$) obtained here are much smaller than the theoretical value of 0.396 nm for Cu_3NAg[4]. This is to say that the Cu_3N lattice serves well as the framework of the deposit. For the Cu_3NM_x deposits with 'x' up to the semiconductor-to-metal transition, the structure of parent Cu_3N lattice with some cell centers occupied by the extra metal atoms can be justified.

References

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2. Suleiman, M. S. H. & D. P. Joubert, Theoretical calculations on the structural, electronic and optical properties of bulk silver nitrides, arXiv:1212.6507v1, and references therein.

3. Pierson, J. F. & Horwat, D. Addition of silver in copper nitride thin films deposited by reactive magnetron sputtering. *Scripta Mater.* **58,** 568-570 (2008).

4. Moreno-Armenta, M. G., Perez, W. L. & Takeuchi, N. First-principles calculations of structural and electronic properties of Cu_3MN compounds with M = Ni, Cu, Zn, Pd, Ag, and Cd. *Solid State Sci.* **9,** 166-172 (2007).