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# Nearly Constant Electrical Resistance over Large Temperature Range in $\text{Cu}_3\text{NM}_x$ ( $M = \text{Cu}, \text{Ag}, \text{Au}$ ) Compounds

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Electrical resistance is a material property that usually varies enormously with temperature. Constant electrical resistivity over large temperature range has been rarely measured in a single solid. Here we report the growth of  $\text{Cu}_3\text{NM}_x$  ( $M = \text{Cu}, \text{Ag}, \text{Au}$ ) compound films by magnetron sputtering, aiming at obtaining single solids of nearly constant electrical resistance in some temperature ranges. The increasing interstitial doping of cubic  $\text{Cu}_3\text{N}$  lattice by extra metal atoms induces the semiconductor-to-metal transition in all the three systems. Nearly constant electrical resistance over 200 K, from room temperature downward, was measured in some semimetallic  $\text{Cu}_3\text{NM}_x$  samples, resulting from opposite temperature dependence of carrier density and carrier mobility, as revealed by Hall measurement.  $\text{Cu}_3\text{NAg}_x$  samples have the best performance with regard to the range of both temperature and doping level wherein a nearly constant electrical resistance can be realized. This work can inspire the search of other materials of such a quality.

Electrical resistance is the most conventional and also the most useful property of a material. The temperature dependence of electrical resistance has to be taken into account when constructing devices and circuits. Remarkably, electrical resistance is a physical property that has an extremely large dynamical range of variation that for a specific material, often an electrical resistance variation by a few orders of magnitude can be measured<sup>1,2</sup>. It is just the easier manipulation of semiconductors' electrical resistance in a large dynamic range that lays the ground for our electronic era<sup>3</sup>. At the other extreme, for many an application electrical resistance that changes only slightly with temperature is also highly desirable. Such devices are usually realized with a few material components and/or in a compensative way, as in the alloy manganin which has to be prepared by a complicated series of heat-treatment. Considering the very large dynamic range of variation for electrical resistance, it would seem impracticable to demand a single solid to manifest a constant electrical resistance over a large temperature range. Yet the possibility of there existing single solids that display a nearly constant electrical resistance, and in a very large temperature range, over 200 K say, cannot be excluded. Intuitively, an indirect band semiconductor that can be modified to manifest semiconductor-to-metal transition arising from doping, by which the conduction band and valence band approach each other and may even cross over, is a good candidate, since when band cross-over occurs, the carrier density and carrier mobility can show an opposite tendency in response to temperature change.

$\text{Cu}_3\text{N}$  is a compound that has attracted much attention because of its potential application in various optical, electrical and magnetic devices<sup>4-7</sup>. Early work was focused on the optimal synthesis and its employment as write-once optical recording media<sup>4,8</sup>. In recently years, some other intriguing applications of  $\text{Cu}_3\text{N}$  thin films or nanocrystals have also been explored, for example, to be used as electrode material in Li-ion batteries<sup>9</sup>, as cathode catalyst in alkaline fuel cells<sup>10</sup>, and as barrier layer in low resistance magnetic tunnel junctions<sup>11</sup>, to name just a few. The resistive-switching behavior in  $\text{Cu}_3\text{N}$  thin films<sup>12</sup>, and the magnetic transition of 3d-metal doped  $\text{Cu}_3\text{N}$  structures<sup>6</sup> are also of great concern in recent research.

The stoichiometric  $\text{Cu}_3\text{N}$  is an indirect-band semiconductor in the cubic anti- $\text{ReO}_3$  type structure with a lattice constant of 0.383 nm (for the lattice structure, see Supplementary Fig. S1). This structure is rather open as the center of the primitive unit cell is vacant, thus it may accommodate another atom of Cu, Ag, Pd, Zn, etc. The interstitially doped  $\text{Cu}_3\text{N}$  serves as a model system for the study of "enclosed atom"<sup>13,14</sup>. With the intercalation of more extra metal atoms in the host lattice, the material will experience a semiconductor-to-metal transition and will immediately turn into semimetallic in character<sup>13,15</sup>. When the doping level just rises over the critical value for transition corresponding to zero-gap, the material will show a very small temperature coefficient of resistance in some region of temperature, as can be conceived from the formula  $\sigma = n_e\mu_e + n_h\mu_h$ , where  $n$  is the carrier density,



and  $\mu$  denotes the carrier mobility. This phenomenon was first confirmed by current authors in  $\text{Cu}_3\text{NPd}_{0.283}$ <sup>5</sup>. So far, the research about the interstitially doped  $\text{Cu}_3\text{N}$  is dominated by theoretical investigations. First-principles calculation of the structural and electronic properties of  $\text{Cu}_3\text{NM}$  compounds (with  $M = \text{Ni}, \text{Cu}, \text{Zn}, \text{Pd}, \text{Ag}$  and  $\text{Cd}$ ) and some experiment results reveal that the incorporation of foreign metal atoms in the cell centers of the cubic lattice modifies the electronic structure of  $\text{Cu}_3\text{N}$  and all such  $\text{Cu}_3\text{NM}$  compounds are metallic<sup>13–15,16</sup>. Notably, report on the synthesis of the samples of well determined composition and atomic structure, and property measurement and mechanism (particularly for electrical transport) discussion based on experimental data are comparatively rare<sup>17,18</sup>. The difficulty lies in the growth of the intercalated samples with a well-preserved  $\text{Cu}_3\text{N}$  host lattice. In fact, even the obtainment of a nearly stoichiometric  $\text{Cu}_3\text{N}$  film is itself a challenge<sup>19</sup>.

In the current work we report the determination of temperature dependence of electrical resistance in the films of  $\text{Cu}_3\text{NM}_x$  ( $M = \text{Cu}, \text{Ag}, \text{Au}$ ), here  $x$  denotes the fraction of the occupied cell centers in the  $\text{Cu}_3\text{N}$  host lattice, which were grown by magnetron (co)sputtering of metal targets in the nitrogen atmosphere. The amount of extra metal atoms incorporated into the  $\text{Cu}_3\text{N}$  lattice, denoted by the parameter  $x$ , was varied from zero to a sufficiently large value till the resulting material is essentially metallic. Samples of nearly constant electrical resistance, which was judged by the variance of the normalized electrical resistivity, in the range from room temperature down to  $\sim 50$  K were obtained. The mechanism was discussed on the basis of measured carrier density and carrier mobility, together with the light absorption spectral data. These results can inspire further work on the search of single solids that will show constant electrical resistance in even larger temperature ranges, which promise more useful engineering applications.

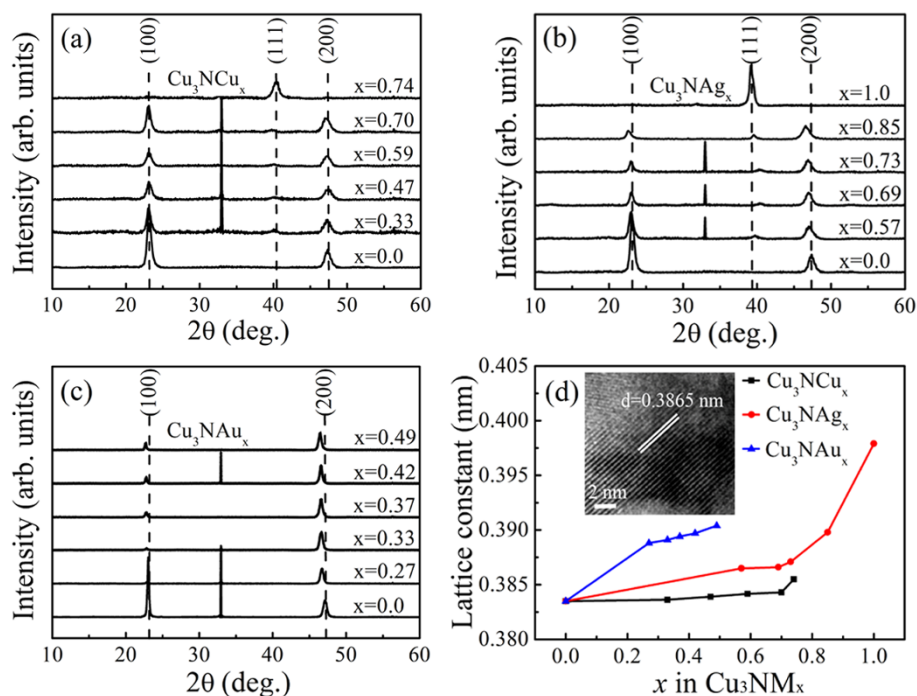
## Results

Thin films of nearly stoichiometric  $\text{Cu}_3\text{N}$  as reference material and  $\text{Cu}_3\text{NM}_x$  ( $M = \text{Cu}, \text{Ag}, \text{Au}$ ) of various compositions, as specified by  $x$  the fraction of the occupied cell centers in the  $\text{Cu}_3\text{N}$  lattice, were grown. From x-ray diffraction (XRD) patterns it can be concluded

that up to a quite large value of doping level, the host lattice of the  $\text{Cu}_3\text{N}$  can be maintained, as confirmed by the characteristic (100)- and (200) reflections of  $\text{Cu}_3\text{N}$  lattice (Fig. 1). When more Cu is interstitially doped into the deposits, the deposits, denoted as  $\text{Cu}_3\text{NCu}_x$ , while maintaining the cubic structure of  $\text{Cu}_3\text{N}$ , reveal an increasing lattice constant from  $a = 0.383$  nm for  $\text{Cu}_3\text{N}$ . From Fig. 1a one sees that, with  $x$  even going up to 0.70, the characteristic (100)- and (200) reflections on the XRD patterns remain well preserved while slightly shifting towards smaller angle. At  $x = 0.74$ , these two peaks disappear, and the (111) reflection emerges instead. At the same time, the lattice constant is dilated to a value of 0.385 nm. The film quality then becomes obviously degraded, i.e., less compact and less adhesive to the substrate, but such deposits are not of interest in the current work.

Similar behavior is expected to be observed in the Ag and Au doped- $\text{Cu}_3\text{N}$  structures. However, unlike in the case of Cu where the extra Cu atoms can be unambiguously attributed to the occupation of the cell centers of the  $\text{Cu}_3\text{N}$  lattice, and the structure can be assuredly specified as  $\text{Cu}_3\text{NCu}_x$ , whether the deposits obtained from co-sputtering of Cu with Ag (Au) can be specified as  $\text{Cu}_3\text{NAg}_x$  ( $\text{Cu}_3\text{NAu}_x$ ), i.e., whether the Ag (Au) atoms occupy uniquely the centers of the unit cells in the  $\text{Cu}_3\text{N}$  host lattice, is a question that needs be clarified. Here we pointed out only that with the XRD patterns (Figs. 1b–1c) and other evidences, the deposits with Ag or Au here concerned can be definitely specified as  $\text{Cu}_3\text{NAg}_x$  or  $\text{Cu}_3\text{NAu}_x$  (for more detailed argument, see supplementary information). In the following discussion such samples are referred to as  $\text{Cu}_3\text{NAg}_x$  or  $\text{Cu}_3\text{NAu}_x$ , bearing in mind that in such materials the possibility of sporadic substitution of Cu atom on some sites by Ag (Au) atom cannot be completely excluded.

In the case of Ag doping, even though the (111) reflection of the  $\text{Cu}_3\text{N}$  lattice already begins to be visible at  $x = 0.57$ , yet up to  $x = 0.85$  the XRD patterns are still dominated by the (100)- and (200) reflections (Fig. 1b). The lattice constant increases monotonically from 0.383 nm for  $\text{Cu}_3\text{N}$  to 0.398 nm for  $\text{Cu}_3\text{NAg}$ . In the case of Au doping, since the Au has a larger ionic radius, the insertion of Au atoms causes severe dilation of the  $\text{Cu}_3\text{N}$  lattice that the shift of the (100)- and (200) reflections is quite obvious (Fig. 1c). We obtained



**Figure 1** | Crystalline structure. (a–c) XRD pattern for the deposits  $\text{Cu}_3\text{NCu}_x$ ,  $\text{Cu}_3\text{NAg}_x$  and  $\text{Cu}_3\text{NAu}_x$ ; (d) Variation of lattice constant with the fraction of occupied cell centers in the  $\text{Cu}_3\text{N}$  lattice. The inset in (d) shows the TEM image of the sample  $\text{Cu}_3\text{NAg}_{0.57}$ .



high-quality  $\text{Cu}_3\text{NAu}_x$  films with  $x$  up to 0.49, all showing well preserved (100)- and (200) reflections characterizing the  $\text{Cu}_3\text{N}$  lattice. In the given range of Au doping, the semiconductor-to-metal transition of interest already occurs in the deposits. The dependence of lattice constant on the fraction of occupied cell centers for the three sample series is summarized in Fig. 1d.

For the nearly stoichiometric  $\text{Cu}_3\text{N}$  sample, its electrical resistance exhibits an exponential growth with decreasing temperature (see Supplementary Fig. S2a), which is typical for an intrinsic semiconductor in which the electronic transport is dominated by thermal activation. This temperature dependence of electrical resistance can be approximated by the equation  $\rho(T) = C \exp(-E_a/kT)$ , with the activation energy  $E_a \sim 0.2$  eV. This  $E_a$  deviates a lot from the  $E_g/2$  in the formula  $\rho = C e^{-E_g/2kT}$  for a perfect intrinsic semiconductor  $\text{Cu}_3\text{N}$  which should have a band gap of  $\sim 1.9$  eV<sup>20</sup>. This weird behavior results from the fact that even the stoichiometric  $\text{Cu}_3\text{N}$  sample is composed of nanocrystallites, generally of  $\sim 40$  nm in size, enclosed by Cu-terminated {111}-planes which provide alternative hopping paths for charge carriers<sup>18</sup>. Largely due to the same reason,  $\text{Cu}_3\text{N}$  is also notoriously known for the vast discrepancy in the reported band gap values. With the incorporation of extra Cu, or foreign atoms Ag or Au, the electrical resistance at room temperature of the samples decreases steadily with increasing  $x$  in  $\text{Cu}_3\text{NM}_x$  ( $M = \text{Cu}, \text{Ag}, \text{Au}$ ) (Fig. 2a), indicating the drastic change in the band structure induced by the interposition of extra atoms into the  $\text{Cu}_3\text{N}$  lattice. The temperature dependence of electrical resistivity for some samples of the  $\text{Cu}_3\text{NM}_x$  ( $M = \text{Cu}, \text{Ag}, \text{Au}$ ) series is displayed in Figs. S2–S4, see the Supplementary information.

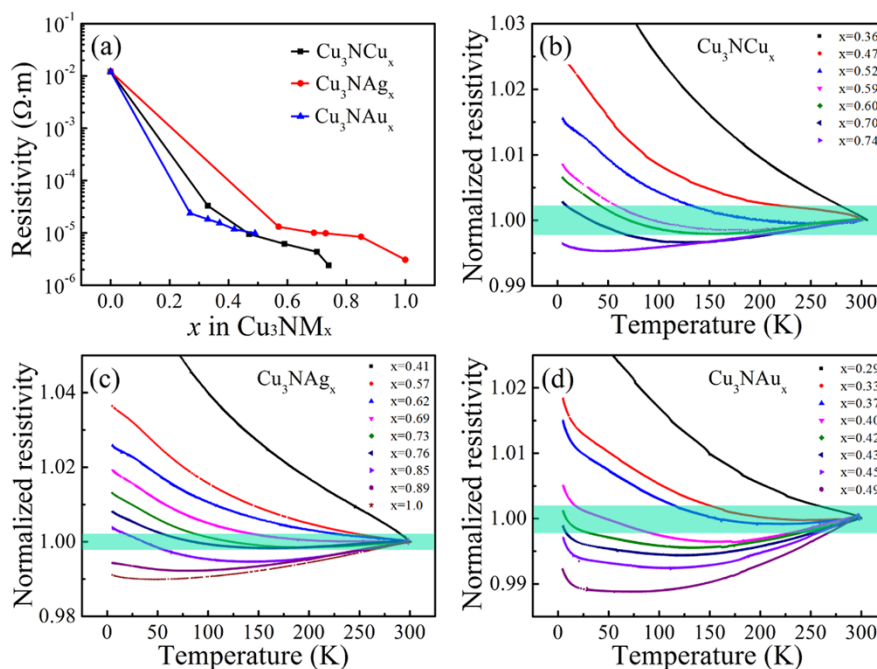
With increasing extra Cu in the deposit, the deposit  $\text{Cu}_3\text{NCu}_x$  reveals a steadily reduced electrical resistance in the temperature range from room temperature down to 5 K. Moreover, for  $x = 0.59$  onward, with decreasing temperature the electrical resistance initially decreases to a minimum and then rises again. In fact, with further increasing  $x$  this minimum shifts steadily towards lower temperature. For the sample  $\text{Cu}_3\text{NCu}_{0.74}$ , the curve reveals typical behavior of a metal, which falls in the regime of conventional Fermi liquid theory<sup>2</sup>, and the minimum appears at  $\sim 40$  K (see Supplementary

Fig. S2 & Fig. 2b). This confirms the occurrence of semiconductor-to-metal transition in  $\text{Cu}_3\text{NCu}_x$  with the doping level in the neighborhood of  $x = 0.59$ .

It is anticipated that at the point of the semiconductor-to-metal transition, in fact when the material is slightly more at the metal side, thus the indirect-band semiconductor has turned into a semimetal<sup>13,14</sup>, the electrical resistance may be less sensitive to temperature change, as the opposite tendency of variation for carrier density and carrier mobility in this situation may compensate each other to some extent. Fig. 2b shows the temperature dependence of electrical resistance normalized against the values at room temperature for samples  $\text{Cu}_3\text{NCu}_x$  with  $x$  ranging from 0.36 to 0.74 (noting that the electrical resistance at room temperature decreases to  $2.3 \times 10^{-6} \Omega \cdot \text{m}$ , see Fig. 2a). It can be seen that for the sample  $\text{Cu}_3\text{NCu}_{0.60}$ , in the temperature range from room temperature down to 40 K, i.e., within a temperature range of 260 K, the normalized electrical resistance varies within the range of  $\pm 0.002$ , and the variance, defined as  $\Delta\rho = \sqrt{\frac{1}{n} \sum_i (\rho(T_i) - \bar{\rho})^2}$ , where  $\bar{\rho} \sim 1.0$  is the averaged value of the normalized electrical resistance, is only  $8.6 \times 10^{-4}$ .

Fig. 2c displays the temperature dependence of the normalized electrical resistance for samples  $\text{Cu}_3\text{NAg}_x$  with  $x$  ranging from 0.41 to 1.0 (At the same time, the electrical resistance at room temperature decreases to  $3.0 \times 10^{-6} \Omega \cdot \text{m}$  for  $\text{Cu}_3\text{NAg}$ ). Remarkably, the electrical transport behavior for the sample  $x \sim 0.85$  is typically metallic. For the sample with  $x \sim 0.76$  which is slightly larger than  $x \sim 0.73$  where the semiconductor-to-metal transition just occurs, the normalized electrical resistance varies within  $\pm 0.002$  in the temperature range from room temperature down to 55 K, and the variance of the normalized electrical resistance in this temperature range as large as 245 K is only  $8.0 \times 10^{-4}$ .

In comparison to cases of Cu and Ag insertion, the semiconductor-to-metal transition occurs already at  $x \sim 0.33$  in the  $\text{Cu}_3\text{NAu}_x$  system (Fig. 2d). A very flat variation of electrical resistance with temperature in a range as wide as 100 K was not measured. In the sample  $\text{Cu}_3\text{NAu}_{0.37}$ , the variance of the normalized electrical



**Figure 2 | Resistivity characterization.** (a) Electrical resistance at room temperature for the deposits of  $\text{Cu}_3\text{NCu}_x$ ,  $\text{Cu}_3\text{NAg}_x$  and  $\text{Cu}_3\text{NAu}_x$  of various doping levels  $x$ ; (b–d) Temperature dependence of the normalized electrical resistivity for the sample series of  $\text{Cu}_3\text{NCu}_x$ ,  $\text{Cu}_3\text{NAg}_x$  and  $\text{Cu}_3\text{NAu}_x$ , respectively.



resistance in the range from room temperature to 150 K measures  $3.3 \times 10^{-4}$ . The scenario that the normalized electrical resistance varies within  $\pm 0.002$  in a temperature range over 200 K was not measured in this system.

By comparing the temperature dependence of the normalized electrical resistivity for the three sample series, it can be said that the  $\text{Cu}_3\text{NAg}_x$  structure makes the best performance to provide nearly constant electrical resistivity in wide temperature range, considering both the smallness of variance of the electrical resistivity and the range of temperature within which the measurement was made.

## Discussion

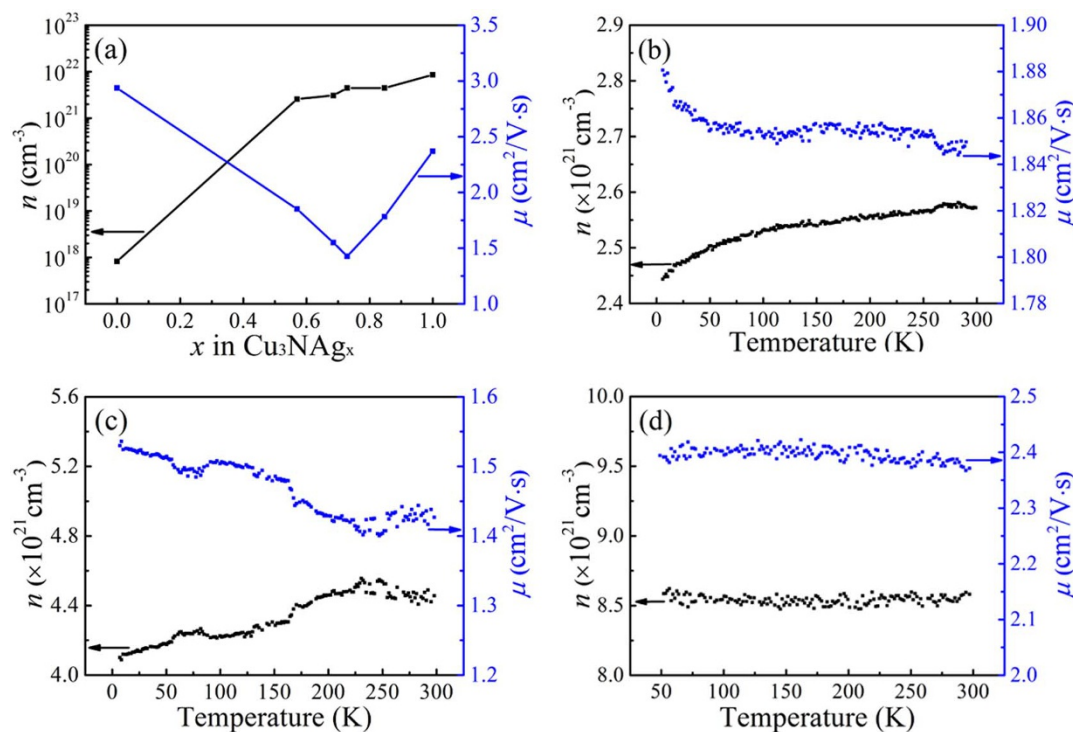
The temperature dependence of the electrical resistivity confirms that the interstitial doping of the  $\text{Cu}_3\text{N}$  lattice turns  $\text{Cu}_3\text{NM}_x$  ( $M = \text{Cu}, \text{Ag}, \text{Au}$ ) gradually to be metallic when  $x$  increases over a critical value. As speculated by theoretical simulation, in this process the intercalated structures will show a narrowing band gap, which can be revealed by the optical absorption spectrum. Taking the series of  $\text{Cu}_3\text{NAg}_x$  for instance, the samples with  $x$  up to 0.57 shows perfect linearity in the  $(\alpha h\nu)^{1/2}$  vs.  $h\nu$  curves, pointing towards a continuously narrowing band-gap (see Supplementary Fig. S5). At  $x = 0.73$ , the deposit has a zero band-gap, and since then on the deposits become metallic. At the doping level slightly larger than the critical value for the transition, the conduction band and the valence band may become overlapped.

The occupation of the cell centers of the  $\text{Cu}_3\text{N}$  lattice by extra Au, Ag, Cu atoms, when the doping is not so heavy, turns the derived structures into a n-type semiconductor, as confirmed by the negative Hall coefficient. Since in the  $\text{Cu}_3\text{NM}_x$  compounds the conduction, albeit ambipolar in fact, is dominated by electrons provided by excessive metal atoms, we can assume that  $n_e\mu_e$  is considerably larger than  $n_h\mu_h$  so as to roughly estimate the electron density and mobility from the measured electrical resistivity and Hall coefficient. As anticipated, with the insertion of more extra Au, Ag, and Cu atoms,

the carrier density at room temperature increases monotonically. Taking  $\text{Cu}_3\text{NAg}_x$  as example, the carrier density jumps from  $7.0 \times 10^{17}/\text{cm}^3$  at  $x = 0.0$  to  $8.6 \times 10^{21}/\text{cm}^3$  when  $x$  approaches 1.0. In contrast, the carrier mobility shows a minimum at  $x \sim 0.73$  where the structure may show a maximum disorder due to the insertion of extra metal atoms into the host lattice (Fig. 3a). The quantitative detail is difficult to be specified since the mobility depends strongly on the quality of the individual samples. In  $\text{Cu}_3\text{NCu}_x$  and  $\text{Cu}_3\text{NAu}_x$  where the  $x$  value is not very large, the mobility decreases monotonically with  $x$  in the given range. By the way, it is remarkable that samples such as  $\text{Cu}_3\text{NAg}_x$  with large  $x$  value have a carrier density comparable with metal, albeit they show a temperature dependence of electrical resistivity typical for semiconductor. The reason lies in the fact that in conventional semiconductors such as n-type Si, the carrier is provided by ionized impurity atoms occupying lattice sites, of which the density is consequently rarely higher than  $10^{21}/\text{cm}^3$ . However, in  $\text{Cu}_3\text{NM}_x$  it is the excessive metal atoms, the electrons can freely dissociate from such parent atoms, that occupy the originally vacant cell centers of the cubic lattice, which modify the band structure towards a narrower gap till eventually becoming fully metallic<sup>13</sup>, and at the same time contribute a large amount of carriers.

From Fig. 3b it can be seen that in a particular doped specimens,  $\text{Cu}_3\text{NAg}_{0.57}$  for instance, the carrier density becomes less with decreasing temperature, while the carrier mobility shows a reversed tendency, a favorable condition for having a slowly varying product of carrier density and carrier mobility. For the sample  $\text{Cu}_3\text{NAg}_{0.73}$ , although the data become more scattering, the same tendency is observed, and for both carrier density and carrier mobility the amplitudes of variation in the given temperature range become abated, which then result in a only slightly varied product, as also confirmed by the temperature variation of the electrical resistance (Cf. Fig. 2c).

That the product of carrier density and carrier mobility from the Hall measurement (Figs. 3b–3d) is not consistent with the electrical resistance is due to the fact that the electrical conductivity is



**Figure 3 | Electronic transport measurement.** (a) The variation of carrier density and carrier mobility with  $x$ , the fraction of occupied cell centers, in  $\text{Cu}_3\text{NAg}_x$ ; (b–d) The temperature dependence of carrier density and carrier mobility in the samples  $\text{Cu}_3\text{NAg}_{0.57}$ ,  $\text{Cu}_3\text{NAg}_{0.73}$  and  $\text{Cu}_3\text{NAg}_{1.0}$ , respectively.



contributed by both electrons and holes, whereas the contribution of the minor carrier (here the hole) to the Hall measurement is not accounted for in the same way as to the electrical resistance. The scattering of carriers by phonons of an imperfect lattice, in which the center of the cubic unit cells is randomly and partially occupied, is believed to be the controlling mechanism for electrical resistivity. For the deposits here concerned, which comprise of Cu-enclothed nanocrystallites, the “variable range hopping” among the nanocrystallites<sup>21</sup>, i.e., the charges’ quantum tunneling between localized sites, is also a governing mechanism that may also demonstrate its effect in the temperature dependence of electrical resistance. Anyway, in spite of these disturbing factors that contribute to the electrical resistance, it can be confirmed that at the neighborhood of transition in the  $\text{Cu}_3\text{NCu}_x$  and  $\text{Cu}_3\text{NAg}_x$ , a nearly constant resistance is obtainable in a large temperature range over 200 K. The detailed quantitative investigation into the mechanism can be better realized in materials having a better crystallinity, which is now strived for in our laboratory.

In summary, thin films of the compounds  $\text{Cu}_3\text{NCu}_x$ ,  $\text{Cu}_3\text{NAg}_x$  and  $\text{Cu}_3\text{NAu}_x$  were synthesized by magnetron sputtering of metal targets in nitrogen atmosphere. The increasing fraction of occupied cell centers in the host  $\text{Cu}_3\text{N}$  lattice by extra Au, Ag or Cu atoms induces the semiconductor-to-metal transition in these solids. At the metallic side not far from the semiconductor-to-metal transition, the carrier density in the samples increases with the increasing temperature due to the thermal excitation, while the carrier mobility declines due to the more violent lattice scattering among others. This brings about the possibility of obtaining some single solids of nearly constant electrical resistance over a large temperature range, which has been observed in all the  $\text{Cu}_3\text{NCu}_x$ ,  $\text{Cu}_3\text{NAg}_x$  and  $\text{Cu}_3\text{NAu}_x$  systems. Remarkably, the sample  $\text{Cu}_3\text{NAg}_{0.76}$ , the variance of the normalized electrical resistivity, in a temperature range from room temperature to 55 K, is only  $\sim 8.0 \times 10^{-4}$ . As for the transport mechanisms, thermal activation and variable hopping range dominate the semiconductor state, while Fermi liquid theory can account for the metal state. The current research has verified the possibility of obtaining nearly constant electrical resistivity in single solids, and offers clues of finding more such materials in even larger temperature ranges, and better if extended farther above the room temperature. Single solids of such a quality are highly desirable in the fabrication of precision resistors and other devices based on them that are to be used in environment of variable temperatures.

## Methods

**Film preparation.**  $\text{Cu}_3\text{NM}_x$  ( $M = \text{Cu, Ag, Au}$ ) films were prepared onto c-Si and quartz substrates in a custom-designed radio-frequency (27.12 MHz) reactive magnetron sputtering system, with high purity (5 N) nitrogen as the working gas. In order to obtain  $\text{Cu}_3\text{NAg}_x$  and  $\text{Cu}_3\text{NAu}_x$  samples of various doping levels, chips of Au or Ag metal in a size of  $2 \times 2$  mm were placed in a symmetrical way onto the ring-formed sputter region of the Cu target. The content of Ag or Au in the ternary deposits can be adjusted by changing the number of the metal chips on the Cu target and/or slightly varying their positions with regard to the sputtered region, while for the case of Cu doping this was realized via adjusting the ratio of nitrogen versus argon in the working gas. Before mounting into the chamber, the substrates were ultrasonically cleaned in acetone, alcohol and deionized water, successively. The working parameters are as follows: The target-substrate distance was 50 mm, the working pressure in the chamber was kept at 1.3 Pa, and the RF power was tuned to 60 W. The procedure of obtaining nearly stoichiometric  $\text{Cu}_3\text{N}$  samples and control of sample composition was described in our previous publications<sup>18,19</sup>.

**Characterization.** The surface morphology of the as-deposited films was evaluated by using a scanning electron microscope (XL30 S-FEG), and the film thickness was determined by a Talystep profilometer (Veeco Dektak 8). The crystal structure of the as-deposited films was characterized by using X-ray diffraction (XRD, Ultima IV, Rigaku) with the  $\text{Cu K}\alpha$  line. More information concerning the precise determination of the lattice constant in the deposits was obtained by using a high-resolution transmission electron microscope (TEM, JEOL 2010). X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi, Thermo Scientific) measurement was used to determine the chemical bonding states and composition of the deposits. The sample composition determination was done with the nearly stoichiometric binary  $\text{Cu}_3\text{N}$  as reference. Temperature dependence of electrical

resistance and Hall effect under a magnetic field of 5 Tesla were measured in the temperature range from room temperature down to 5 K by employing the five-contact method in a physical property measurement system (PPMS 6000, Quantum Design). The resistivity was determined by using the conventional four-point probe collinear technique, while the Hall measurement was made in a geometry with the four contacts on the corners of a square. The optical gap of the deposits was evaluated on the basis of the absorption data recorded by a UV-Vis spectroscopy (SP2500i, Princeton instruments). For the PPMS measurement, thinner films ( $\sim 60$  nm in thickness) were used, while for XRD characterization the samples are generally as thick as  $\sim 1.0$   $\mu\text{m}$ .

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## Author contributions

Z.X.C. and A.L.J. initiated the current research; N.P.L. performed the experiment; Z.X.C. compiled the manuscript; all the authors contributed to analysis of the results.

## Additional information

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