

Ternary Cu_3NPd_x exhibiting invariant electrical resistivity over 200 K

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Electrical resistivity is a physical property of enormous importance, but it is usually a complicated function of temperature. Here the authors report a vanishing temperature coefficient of electrical resistance ($<3.0 \times 10^{-6}/\text{K}$) in the temperature range from 240 to 5 K measured in $\text{Cu}_3\text{NPd}_{0.238}$, following the semiconducting-to-semimetallic transition in Cu_3NPd_x with x increasing from zero. It results from a delicate balance between the opposite changes of the number of carriers and the carrier mobility with temperature, which is possible only in a semimetal. This finding will inspire the search for similar materials and promote an in-depth investigation of the detailed operating mechanism. © 2006 American Institute of Physics. [DOI: 10.1063/1.2422882]

Solid materials that exhibit some physical properties nearly invariant over a substantial temperature range can be very useful for applications. One renowned example is the alloy Invar which has a low and linear coefficient of thermal expansion ($\sim 10^{-6}/\text{K}$ at room temperature), thus it has been widely applied in the realization of measuring and/or alignment functions and beyond.¹ Electrical resistivity is a physical property of enormous importance, both for the understanding of solids and for their actual applications. The electrical resistivity of solids, apart from the possibility of superconductivity, can vary in a range of 10^{32} which may be the widest of any common physical property of solids.² It is generally a sensitive function of temperature that even for an individual metal the electrical resistivity may differ by a few orders of magnitude when cooling from room temperature down to the temperature of liquid helium (~ 4 K). Moreover, the temperature dependence of the electrical resistivity behaves quite irregular, since various different mechanisms, including the phonon scattering, impurity and defect scattering, mutual scattering of electrons, and so forth, are involved in the electrical transport in different temperature ranges.^{2,3} This explains why it is quite unlikely, if not absolutely impossible, to fabricate a single solid of vanishing temperature coefficient of resistance (TCR) in a considerable temperature range—the temperature-insensitive resistors demanded in many critical applications hitherto have to be realized via a compensation mechanism in designed material structures or circuits. A lot of innovative applications can be conceived for any individual solid of invariant electrical resistivity. By studying the semiconducting-to-semimetallic transition⁴ of the composition-modulated Cu_3NPd_x thin films, we found that a vanishing TCR in the range from 240 K down to 5 K could be measured in $\text{Cu}_3\text{NPd}_{0.238}$.

Thin films of Cu_3N and Cu_3NPd_x ($0 < x < 0.350$) were prepared on the Si (001) wafers by reactive magnetron sputtering of Cu and Pd targets (4N purity) with nitrogen. In order to obtain a single-phased compound sample without any excessive metal nanoparticles, a low substrate temperature (~ 100 °C) in combination with a small power supply (<150 W), consequently a low ion energy for the bombard-

ment of the targets, and a high working pressure (>0.7 Pa) are favorable.⁵ Chemical analysis together with the morphology examination was performed on a scanning electron microscope (XL30 S-FEG) equipped with an energy-dispersive x-ray spectrometer. A transmission electron microscope (CM200 FEI) and an x-ray diffractometer (Rigaku D/Max-2400) were employed for the structural characterization. The temperature dependence of the electrical resistivity was measured in a physical properties measurement system (Quantum Design) by using the conventional four-probe method.

The host material Cu_3N in the cubic anti- ReO_3 lattice is a typical semiconductor with an indirect band gap of ~ 1.9 eV.^{6–9} Due to the weak Cu–N bonding that facilitates nitrogen reemission from the compound, the Cu_3N samples generally show some deficiency of nitrogen; consequently they display electronlike conductivity as confirmed by the negative Hall coefficient. By careful control of the processing parameters, nearly stoichiometric, single-phased Cu_3N thin films can be obtained with a carrier density being brought down to below $3.0 \times 10^{18}/\text{cm}^3$. The open structure of the Cu_3N lattice can accommodate another metal atom to form compounds such as Cu_4N or the ternary Cu_3NPd .^{10,11} Remarkably, Cu_3NPd is a semimetal due to the intersection of the energy bands at the Fermi level.¹⁰ Consequently, a semiconducting-to-semimetallic transition is anticipated in the off-stoichiometric Cu_3NPd_x when x increases continuously from zero to unity.

The interposition of metal atoms at the center of the cubic Cu_3N lattice severely deteriorates the covalent bonding in the resulting materials that the compounds Cu_4N and Cu_3NPd are only a theoretical being. In fact, the largest reported value of x never exceeds 0.989 whereupon the compound exists in fine powders.¹¹ We found that those Cu_3NPd_x thin-film samples with $x > 0.5$ show a very poor crystallization, therefore we restrict our discussion to the samples with $0.0 \leq x \leq 0.350$ which are well crystallized as confirmed by both x-ray diffraction patterns and transmission electron micrographs (Figs. 1 and 2). For the sample containing only a tiny amount of Pd, e.g., $\text{Cu}_3\text{NPd}_{0.048}$, the x-ray diffraction pattern remains unchanged as that of the host Cu_3N lattice showing only the (001) and (002) reflections. When the Pd concentration is large enough ($x \geq 0.175$), the (001) reflection was replaced by the strong (111) reflection which becomes deteriorated both in intensity and in spectral profile

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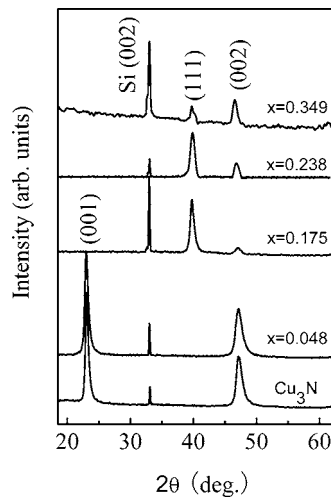


FIG. 1. X-ray diffraction patterns of Cu_3NPd_x with varying x values.

for samples with more Pd contents (Fig. 1). We can say with confidence that the Cu_3NPd_x thin films here concerned with $x < 0.35$ are crystalline. The addition of Pd atoms results in a slightly enlarged lattice constant which increases from $a = 0.383 \text{ nm}$ for the pure Cu_3N to $a = 0.385 \text{ nm}$ for $\text{Cu}_3\text{NPd}_{0.175}$ [Figs. 2(a) and 2(b)]. The Cu_3NPd_x samples obviously have a better electrical conductivity which in turn results in an improved image quality for the transmission electron micrograph. The fact that the Cu_3NPd_x is metallic at sufficiently large x values, while Cu_3N is semiconducting, may suggest that the interposition of Pd atoms only alter the energy bands near the Fermi surface.⁹

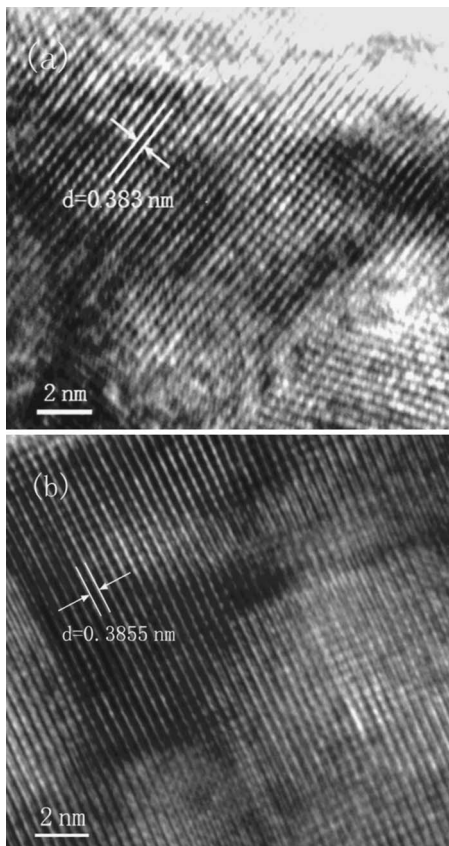


FIG. 2. High-resolution transmission electron micrographs for the stoichiometric Cu_3N (a) and the sample $\text{Cu}_3\text{NPd}_{0.175}$ (b).

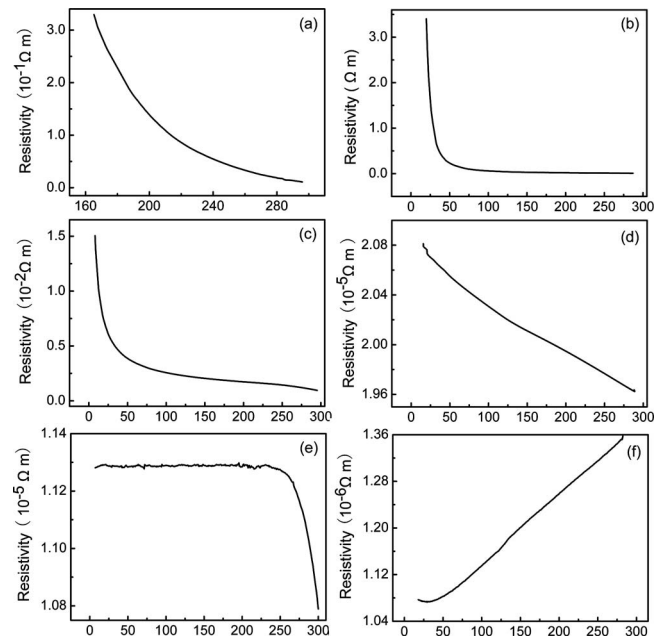


FIG. 3. Temperature (in unit of K) dependence of the electrical resistivity measured in crystalline Cu_3NPd_x thin films. (a) $x = 0.0$, (b) $x = 0.048$, (c) $x = 0.071$, (d) $x = 0.175$, (e) $x = 0.238$, and (f) $x = 0.349$. From (b) to (f), the electrical resistivity at room temperature is reduced by four orders of magnitude.

Figure 3 displays the temperature dependence of the electrical resistivity for the nearly stoichiometric Cu_3N and for the different ternary Cu_3NPd_x compounds. Upon cooling from room temperature, the electrical resistivity of intrinsic Cu_3N rises rapidly [Fig. 3(a)]. This observation is consistent with the wide-band-gap nature of this semiconducting material.^{3,9} The insertion of Pd atoms confers Cu_3NPd_x an improved electrical conductivity owing to the narrowed band gap. Even with a tiny amount of Pd insertion as in the samples with $x = 0.048$ and $x = 0.071$, the rapid onset of resistivity upon cooling is shifted to below 50 K, indicating a narrowed band gap for the current samples [Figs. 3(b) and 3(c)]. A further addition of Pd atoms initiates the semiconducting-to-semimetallic transition that TCR changes its sign. For $\text{Cu}_3\text{NPd}_{0.175}$, its electrical resistivity rises roughly linearly with decreasing temperature in a range as wide as 270 K, and the TCR is -0.00039 K^{-1} [Fig. 3(d)]. Taking $T = 280 \text{ K}$ as the reference point, the resistance over such a broad temperature range changes only by $\sim 5.0\%$. The resistivity for $\text{Cu}_3\text{NPd}_{0.349}$ also displays a good linearity from 50 to 280 K, but now the TCR is 0.00117 K^{-1} [Fig. 3(f)], indicating unambiguously that now the compound has turned to be metallic. In between these two cases of opposite tendencies for the variation of the electrical resistivity with temperature, we may expect a vanishing TCR over a considerable temperature range at some an x value. This occurs in the sample $\text{Cu}_3\text{NPd}_{0.238}$. From 240 K down to 5 K, the TCR is nearly zero ($< 3.0 \times 10^{-6} / \text{K}$), and the relative variance of the electrical resistivity in this temperature range measures as small as 1.42×10^{-5} [Fig. 3(e)].

The temperature dependency of the electrical conductivity for solids is susceptible to many influencing factors; no hard-and-fast rules are available. For a semiconductor, the electrical conductivity can be formally written as $\sigma = e(n_e\mu_e + n_h\mu_h)$, where e and h denote electron and hole, while n and μ stand for the carrier density and carrier mobility, respec-

tively. Both the carrier mobility and the carrier density, or the number of the carriers, are temperature dependent,¹² yet the temperature dependence of the electrical conductivity is dominated by that of the latter, since the mobility changes only in a mild way with the lattice temperature while the number of carrier can be an exponential-like function of $1/T$. With decreasing temperature, the number of the carriers decreases while the mobility generally increases,^{2,12} but in different manners, consequently the resulting electrical resistivity is exclusively temperature dependent. For narrow-band-gap semiconductors and semimetals, the situation is more complicated than in the conventional semiconductors like Si or Ge. The carrier distribution function obeys the Fermi-Dirac statistics which in this case cannot be approximated by the Maxwell-Boltzmann formula. Moreover, the conduction band is Kane type that the effective mass of electron, thus the mobility of electron, changes with the carrier density.⁴ The vanishing TCR occurs when this compound has narrowed its band gap to be a semimetal for which the temperature dependence of the number of the carriers becomes rather mild mannered in contrast to the situation in a semiconductor of a finite band gap. It results from a delicate balance between the opposite changes of the number of carriers and of the carrier mobility with temperature, and reasonably it appears only at temperatures below 240 K—at higher temperatures the increasing number of carriers can easily pay off the loss in carrier mobility to give rise to a rapidly decreasing electrical resistivity. The current discovery, though lacking a clear scenario of detailed microscopic processes due to the difficulty in calculating the band structure for the off-stoichiometric compounds as $\text{Cu}_3\text{NPd}_{0.238}$ and in performing Hall measurement for some supplementary information (the difficulty here lies in the poor adhesion of the Cu_3NPd_x films to the sub-

strate and the poor stability of the contacts under the varying low temperatures), does demonstrate the possibility that a balanced change of carrier density and carrier mobility over a wide temperature range is in principle possible in a class of semimetallic materials. Considering the unlikelihood of a temperature-independent electrical resistivity for solids, the current result also bears some significance to solid-state physics. It will inspire the search for similar materials and promote an in-depth investigation of the detailed operating mechanisms.

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