Crystallize it before it diffuses: Kinetic stabilization of thin-film phosphorus-rich semiconductor CuP$_2$

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Numerous phosphorus-rich metal phosphides containing both P-P bonds and metal-P bonds are known from the solid-state chemistry literature. A method to grow these materials in thin-film form would be desirable, since thin films are required in many applications and they are an ideal platform for high-throughput studies. In addition, the high density and smooth surfaces achievable in thin films are a significant advantage for characterization of transport and optical properties. Despite these benefits, there is hardly any published work on even the simplest binary phosphorus-rich phosphides. Here, we demonstrate growth of single-phase CuP$_2$ films by a two-step process involving reactive sputtering of amorphous CuP$_{2+x}$ and rapid annealing in an inert atmosphere. At the temperature required for crystallization, CuP$_2$ tends to decompose into Cu$_3$P and gaseous phosphorus. However, CuP$_2$ can still be synthesized if the amorphous precursors are mixed on the atomic scale and are sufficiently close to the desired composition (neither too P poor nor too P rich). Fast formation of polycrystalline CuP$_2$, combined with a short annealing time, makes it possible to bypass the diffusion processes responsible for decomposition. We find that thin-film CuP$_2$ is a 1.5 eV band gap semiconductor with interesting properties, such as a high optical absorption coefficient (above 10$^5$ cm$^{-1}$), low thermal conductivity (1.1 W/Km), and composition-insensitive electrical conductivity (around 1 S/cm).

I. INTRODUCTION

Phosphorus readily forms homoelement bonds in the solid state. Accordingly, over a hundred phosphorus-rich binary metal phosphides containing both P-P bonds and metal-P bonds have been synthesized in bulk form.$^{1,2}$ Often, these compounds have semiconducting properties and decompose into elemental phosphorus and a metal-rich phosphide (with only metal-P bonds) at high temperatures.$^2$ Thin-film synthesis of P-rich materials would help determine their technological potential and their compatibility with established materials and processes. In addition, growing these materials in thin-film form would be desirable for high-throughput characterization of their properties as a function of composition and process conditions. However, reports of polycrystalline P-rich phosphides as thin films are very scarce and seem to be limited to basic characterization of ZnP$_2$ and CdP$_2$ deposited by evaporation of powders of the pre-synthesized compounds.$^3,4$ Thin-film growth from elemental or gaseous sources would significantly simplify the synthesis process.

Similar to other P-rich phosphides, bulk synthesis of CuP$_2$ as a single-crystal or powder is well established$^5–10$ but there are no reports of thin-film growth. CuP$_2$ is a semiconductor that has been proposed as a solar absorber,$^{11}$ thermoelectric material,$^{12,13}$ electrocatalyst for hydrogen- and oxygen evolution,$^{14}$ and as a component in composite anode materials for Li$^{15–17}$ and Na-based batteries.$^{18,19}$ Although CuP$_2$ has been incorporated in electrochemical devices, its optoelectronic and thermoelectric characterization is incomplete. For example, the optical absorption coefficient of CuP$_2$ crystals has only been measured in the weak absorption region just above its 1.4 eV–1.5 eV band gap,$^8,10$ so it is impossible to evaluate its performance as a light absorber in the visible. For thermoelectric applications, the properties needed to calculate the quality factor $zT$ have only been measured separately on different CuP$_2$ specimens in single-crystal or powder form. A potential method for growing phosphorus-rich phosphide thin films is reactive sputtering. We have recently shown the feasibility of this deposition technique for various metal-rich phosphide compounds.$^{20–22}$

In this work, we demonstrate a relatively simple
two-step process route to grow polycrystalline CuP$_2$ thin films as semiconductors of potential technological interest. First, reactive sputter deposition of amorphous CuP$_{2+x}$ in a PH$_3$-containing atmosphere; second, crystallization by rapid thermal annealing (RTA) in an inert atmosphere. We find that the crystallization step must be kinetically facilitated by employing amorphous precursors of sufficiently similar composition to the desired CuP$_2$ stoichiometry. We investigate the optical properties of CuP$_2$ over a broad spectral range and conduct comprehensive temperature-dependent thermoelectric characterization (including the $zT$ value) up to room temperature. In particular, we find a remarkably high optical absorption coefficient (above $10^5$ cm$^{-1}$ in the visible), low thermal conductivity (1.1 W/Km), composition-insensitive electrical conductivity (1 S/cm) and a moderate native doping density (10$^{15}$ cm$^{-3}$–10$^{17}$ cm$^{-3}$) potentially suitable for photovoltaic applications.

II. RESULTS AND DISCUSSION

A. Structure and bonding

Bonding in CuP$_2$ has some interesting features that are worth a brief analysis. Bulk CuP$_2$ crystallizes in the monoclinic structure shown in Fig. 1, with space group P2$_1$/c.$^7$ The structure consists of alternating sheets of CuP$_4$ tetrahedra and of homoelement-bonded P atoms in planes parallel to (100) (Fig. 1). Each CuP$_4$ tetrahedron shares an edge and three corners with other analogous tetrahedra. The existence of anion-anion bonding is a key qualitative difference between P-rich compounds like CuP$_2$ and most optoelectronic compounds such as III-V and II-VI semiconductors. The generalized 8 – $N$ rule$^{24}$ can then be used to interpret bonding. In this framework, one may assign the −1 oxidation state to one half of the P atoms, since they are bonded to two other P atoms and three Cu atoms. The remaining P atoms have three P-P bonds and one Cu-P bond and are formally neutral, as the three homoelement bonds complete their octet. To achieve charge neutrality, Cu should then be in the +1 oxidation state. While explicit calculations$^{12}$ indicate that only about 30% of this charge is actually transferred to P due to significant covalency, they also confirm that the charge is only accepted by the P atoms that are in the −1 oxidation state. Thus, CuP$_2$ can be considered a relatively rare example of a compound with mixed anion valence.

Another peculiar feature of the P2$_1$/c structure of CuP$_2$ is that pairs of Cu atoms are quite close to each other (2.48 Å).$^7$ Comparing this distance to the metallic and covalent radii of Cu suggests that some metallic Cu-Cu bonding is to be expected, which is confirmed by calculation of the electron localization function.$^{25}$ These Cu-Cu dimers were recently shown to vibrate anharmonically as a rattling mode and strongly scatter acoustic phonons.$^{25}$ This is the key feature enabling low lattice thermal conductivity in CuP$_2$ in spite of its relatively high acoustic conductivity, thus making it interesting for thermoelectrics.

B. Synthesizability

CuP$_{2+x}$ thin films with a broad range of $x$ (positive and negative) could be deposited by reactive sputtering in a PH$_3$/Ar atmosphere at room temperature, using either a Cu target, a Cu$_3$P target, or both at the same time (see the Experimental Details and the $x$-axis in Fig. 2(a)). The main available parameters to tune $x$ are the RF power on the targets and the PH$_3$ partial pressure (see Supporting Information). Decreasing the power led to higher P contents due to a more P-enriched target surface and/or to a lower flux of Cu at the substrate, promoting phosphorization at the substrate. Higher PH$_3$ partial pressures can be achieved by increasing the total pressure or the PH$_3$ concentration in Ar. Because the PH$_3$ concentration was limited to below 5% in our setup, we had to employ a relatively high sputter pressure (2 Pa $\approx$ 15 mTorr) to obtain films of CuP$_2$ stoichiometry. The wide tunability of the P content in Cu-P films was also observed in our recently reported amorphous B-P films by reactive sputtering.$^{21}$ This compositional flexibility is likely related to the ability of P to form homoelement bonds in the films and segregate as an elemental impurity.

As-deposited CuP$_{2+x}$ films did not exhibit any x-ray diffraction (XRD) peaks, so we crystallized them in an RTA furnace at atmospheric pressure under a N$_2$ flow. Loss of phosphorus at moderate temperatures is a well-known phenomenon in many P-rich phosphides.$^2$ We also observed P losses in all our post-annealed CuP$_2$ films (Figs. 2(a,b)). However, the dependence of these P losses on the initial composition of the as-deposited films is not trivial. In Fig. 2(a) we compare the P/Cu ratio before and after annealing at 400°C for 5 min for various initial compositions between CuP$_{1.3}$ and CuP$_{4.5}$. The P/Cu...
ratio is measured by x-ray fluorescence (XRF) so it represents an average through the depth of the film. Several interesting trends can be identified. First, thicker films generally experience milder P losses, since P losses are too P-rich require solid-state diffusion to form a crystalline CuP₂ phase because Cu atoms are too far apart in the initial amorphous phase. This Cu diffusion process competes against the tendency of P to evaporate due to the weakness of P-P bonds. As a result, P losses are much faster. These findings are summarized in the qualitative diagram shown in Fig. 3.

To visualize the P loss process, we image a film with final composition CuP₁.₃ by scanning electron microscopy (SEM, Fig. 4). Two phases can be clearly distinguished on the micrometer scale: a porous polycrystalline matrix with grain size around 30 nm and islands of more compact morphology. The intensity ratio between the Cu and the P peaks in energy-dispersive x-ray spectroscopy (EDX) increases by a factor ~ 5.5 when moving from the matrix to the islands (Fig. S1, Supporting Information). Thus, we conclude that the matrix consists of CuP₂ and the islands consist of Cu₅P. The mechanism of conversion from CuP₂ to Cu₅P appears to be diffusion of Cu in the plane of the substrate, contributing to the enlargement of seed Cu₅P islands. At the same time, P gradually evaporates elsewhere.

Fig. 2(b) shows the effect of annealing temperature and time on the final composition. As expected, increasing the annealing time at fixed temperature results in more severe P losses (compare the data from 30 s versus 5 min annealing time at 400°C). In general, longer annealing times can be tolerated at lower annealing temperatures. For example, annealing at 350°C for 15 min yields about as many P-poor samples as the case of annealing at 400°C for 5 min. Note that the spread of final P/Cu ratios sometimes obtained for films of otherwise similar initial P/Cu ratios and thicknesses is mainly caused by the different positions of the samples inside the furnace. The samples located further downstream with respect to
FIG. 3. Qualitative convex hull of Cu-P system at two different temperatures. Among competing phases, only Cu$_3$P and the elements are considered. At 0 K, the Gibbs free energy only consists of enthalpy $H$, so the convex hull is drawn following DFT enthalpy calculations as available on the Materials Project database.\textsuperscript{26} Cu$_3$P is found to be a stable phase (on the convex hull) and Cu$_3$P is slightly metastable (above the convex hull). At 700 K, our experiments indicate that Cu$_2$P is destabilized. Part of the reason may be a large entropic term $TS$ for elemental P, which is in gaseous form at this temperature. When higher-energy amorphous precursors (diamond data points) are rapidly heated to 700 K, decomposition into Cu$_3$P and gaseous P is thermodynamically favored. However, Cu$_2$P formation is kinetically facilitated when the initial composition of the precursors is sufficiently close to the Cu$_2$P stoichiometry (red diamond).

The gas flow tend to lose less P, possibly because they are exposed to a finite P partial pressure due to P evaporating from the samples further upstream.

We observe a decrease in the apparent heat capacity of an as-deposited Cu$_{2.5}$P film at around 300 °C by nanocalorimetry (Fig. 2(c)). This indicates an exothermic signal, which may be related to the transition from the amorphous to the (more stable) polycrystalline state. The heat capacity baseline needed to calculate the heat of crystallization is not straightforward to define. If we assume the baseline shown in Fig. 2(c), we estimate the crystallization energy of Cu$_2$P as 13 meV/atom. Although the uncertainty on this value is substantial, some qualitative conclusions can still be drawn. The calculated formation enthalpy of Cu$_2$P from the elements in their standard state is 112 meV/atom.\textsuperscript{26} Since this value is much larger than the estimated crystallization energy, most of the formation energy has probably already been released during formation of the amorphous compound. The thermal energy of a solid at 400 °C is approximately $3kT = 174$ meV/atom using the Dulong-Petit law. Thus, the extra stabilization achieved by crystallizing Cu$_2$P is only a small fraction of the thermal energy available at that temperature.

It is also interesting to consider typical values for the calculated energy difference between the most stable amorphous configuration and most stable crystalline polymorph for a given material. This quantity has been calculated in a previous study for 41 material systems (mainly oxides) at 0 K.\textsuperscript{28} The energy difference varies between $\sim 50$ meV/atom and $\sim 500$ meV/atom depending on the material. The significantly lower crystallization energy measured in Cu$_2$P could indicate that the entropic contribution to the total energy is substantially higher in the amorphous state than in the crystalline state at finite temperatures. Higher entropy is indeed expected in the amorphous state due to higher disorder, and it would contribute to reducing the energy difference between the amorphous and crystalline state of Cu$_2$P at $\sim 700$ K with respect to 0 K. Although this explanation is plausible, it is also possible that Cu$_2$P and other non-oxide compounds simply exhibit different energetic trends than the computationally investigated selection of compounds. Computational analysis of the energetics of a more diverse range of amorphous material systems would certainly be useful.

C. Stability

Previous work on Cu$_3$P single crystals does not comment on their stability under ambient conditions. Simple observations on our CuP$_{2+x}$ films indicate that the as-deposited amorphous precursors are less stable than polycrystalline CuP$_2$ films after annealing. This may be due to the extra P present before annealing and to the higher energy associated with the amorphous state (Fig. 2(c)). The as-deposited films start to show visual signs of reaction with ambient air a few hours after deposition. Once the films have been annealed, their bulk properties appear to be stable for at least a few days of exposure to ambient conditions. However, their visual appearance and electrical conductivity after several months of storage in a vacuum-packed bag followed by a few days in air are both altered. It is likely that the high sputter pressure necessary to obtain a P/Cu ratio above 2 in our growth setup (see Supporting Information) has a negative influence on stability, because films
sputtered at high pressure are generally more porous and more air sensitive due to their higher surface area.\textsuperscript{29} It is currently not clear if stability issues are a consequence of the porous morphology or if they are an intrinsic feature of CuP$_2$ films. The stability of CuP$_2$ films sputtered at lower pressures or deposited by other techniques should be further investigated.

D. Structural and vibrational properties

In agreement with nanocalorimetry results, the originally amorphous CuP$_{2+x}$ films only begin to show crystalline XRD peaks above 300 °C annealing temperature (Fig. S2, Supporting Information). Beyond this lower limit, it is possible to obtain polycrystalline CuP$_{2+x}$ films in the P2$_1$/c structure under various annealing conditions. As long as the final composition is close to the nominal CuP$_2$ stoichiometry, XRD patterns of films processed under different annealing conditions are rather similar (Fig. S2, Supporting Information). When the final P/Cu ratio is significantly less than 2, XRD peaks associated with Cu$_3$P in the hexagonal P6$_3$cm structure begin to appear (Fig. S2, Supporting Information). As an example, the XRD pattern of a CuP$_2$ film annealed at 450 °C for 30 s (Fig. 5(a)) contains all the peaks expected for the P2$_1$/c structure, without major preferential orientation effects and without clear peaks from secondary phases above the noise level.

The Raman spectrum of the same sample is plotted in Fig. 5(b). The phonon density of states (DOS) of CuP$_2$, as calculated by density functional perturbation theory in good agreement with recent experiments,\textsuperscript{25} is also shown for comparison.\textsuperscript{26,30,31} Since Raman spectra of bulk CuP$_2$ are not available in the literature, we briefly discuss some qualitative aspects here. Raman features originating from the phonon bands centered around 300 cm$^{-1}$ and 450 cm$^{-1}$ can clearly be seen in the experimental spectrum. In particular, the most intense Raman peak at 425 cm$^{-1}$ probably arises from one of the lowest-energy phonon branches within the highest-energy band in the calculated DOS. All modes in this band essentially involve vibrations of P atoms with nearly static Cu atoms. The lower the phonon energy, the larger the contribution from Cu vibrations, as expected from the larger mass of Cu.

Since the film is polycrystalline, there are selection rules for Raman-active phonon modes and the Raman spectrum will not directly reflect the phonon DOS. Specifically, all atoms in CuP$_2$ are at 4e Wyckoff positions of the P2$_1$/c space group, so only the A$_g$ and B$_g$ modes are Raman-active according to the character tables.\textsuperscript{32} With a 12-atom unit cell, the total number of Raman-active modes is (12 − 1) × 2 = 22. Eight peaks can be identified the experimental spectrum (Fig. 5(b)). The Cu-Cu rattling mode identified by Qi et al.\textsuperscript{23} as an important scatterer of heat-transporting phonons\textsuperscript{23} is either symmetry-forbidden or too low in intensity to be distinguished by Raman spectroscopy.

E. Electrical and optical properties

The room-temperature electrical conductivity of post-annealed polycrystalline films in the CuP$_{2.0}$ − CuP$_{2.2}$ composition range is between 0.5 S/cm and 1.0 S/cm at room temperature, without a clear dependence on the P/Cu ratio (Fig. 6(a)). The conductivity generally increases with increasing annealing temperature, regardless of annealing time (Fig. S4, Supporting Information). Previously reported conductivities of CuP$_2$ single crystals range from 0.01 S/cm to 30 S/cm, presumably due to differences in the crystal quality.\textsuperscript{5,8–10} Films with severe P losses have significantly higher conductivities (Fig. 6(a)), probably due to the presence of the highly conductive Cu$_3$P phase.\textsuperscript{6} The Seebeck coefficient measured on a freshly annealed CuP$_{2.0}$ film is (+390 ± 10) µV/K (Fig. S3, Supporting Information), indicating native p-type doping. All previously reported
CuP₂ single crystals were also p-type with higher Seebeck coefficients in the 690 μV/K–820 μV/K range. The work function, measured with a Kelvin probe in air on a freshly annealed CuP₂₀ film, is (5.0 ± 0.1) eV.

CuP₂ is a relatively strong absorber of light. Its absorption coefficient α reaches 10⁶ cm⁻¹ at a photon energy hν = E₂ + 0.6 eV above its band gap E₂ = (1.5 ± 0.1) eV (Fig. 6(b)). This compares favorably even with the most efficient direct gap photovoltaic absorbers such as GaAs, CdTe, and CH₃NH₃PbI₃ (MAPI).³³ In fact, the absorption coefficient is as high as in some exciton-enhanced photoabsorbers such as Bi₃ and Cu₂BaSnS₄,³⁴³⁵ indicating that CuP₂ may deserve more detailed optoelectronic characterization. We find that α₁/₂ is linear in photon energy over a 2 eV spectral range above the band gap (Fig. 6(b)), indicating that α ∝ (hν − E₂)². Both the estimated band gap and the spectral dependence of the absorption coefficient are in agreement with previous work on CuP₂ single crystals.⁸⁻¹⁰ Because the α ∝ (hν − E₂)² behavior is often associated with an indirect gap in conventional semiconductors,³⁶ an indirect gap was previously assumed for these CuP₂ crystals.⁸⁻¹⁰

However, there are at least two other factors to consider. (1) The absorption strength of CuP₂ is high even for a direct gap material, so indirect transitions are unlikely to be responsible for it. (2) According to the calculated band structure of CuP₂,²⁶ the fundamental gap should be direct and located between the Γ and the Y point of the Brillouin zone. Two indirect gaps with slightly higher energies exist, due to additional valence band pockets at the X point and between the Y and H points.²⁶ Even though we observe a α ∝ (hν − E₂)² behavior, care should be taken when employing the absorption characteristics typical of Group IV and III-V semiconductors to interpret the nature of the optical transitions of other semiconductors with substantially different band structures. A clear difference between CuP₂ and conventional semiconductors is that the former has many valence- and conduction band pockets at different points of the Brillouin zone. Hence, many different optical transitions can contribute to the overall absorption coefficient. The refractive index of CuP₂ is 3.3–3.4 in the transparent region (Fig. 6(c)). Extrapolation of the real part of the dielectric function to zero photon energy (Fig. S5, Supporting Information) yields a high-frequency permittivity ε∞ = 10.5 ± 1.0. Interestingly, there seems to be a critical P/Cu ratio close to 1, where the electrical and optical properties shift from being “CuP₂-like” (semiconducting and IR-transparent) to being “Cu₃P-like” (metallic and opaque). This transition is manifested by an abrupt change in conductivity (Fig. 6(a)) and visual appearance (inset of Fig. 6(b)).

F. Thermoelectric characterization

We conducted DC and double AC Hall effect measurements, as well as temperature-dependent thermoelectric characterization of three films. They have the following compositions: Cu₄xP₂₀ (labeled “Cu₄−ₓP”), Cu₁₋₃ₓP, and CuP₁₋₁,₅ (labeled “CuPₓ”). We use these labels to emphasize similarity to Cu₃P and CuP₂ as discussed in the previous section. This set of films was deposited on Si₃N₄ membranes as part of a microchip-based thin-film transport characterization platform.³⁷ Differences between this set of films and the films deposited on glass characterized in the rest of the article are listed in the Supporting Information. Since these films have intermediate compositions between CuP₂ and Cu₃P, their prop-

FIG. 6. Room-temperature electrical and optical properties of post-annealed CuP₂₊ₓ films. (a): Electrical conductivity as a function of composition (measured after annealing) and annealing conditions. Films are of comparable thickness except for the P-poor purple data points, which have about half the thickness as the other ones. A zoomed-in view around the CuP₂ stoichiometry is available in Fig. S4, Supporting Information. (b): Absorption coefficient α of a post-annealed CuP₂₀ film together with a α₁/₂ plot versus photon energy. Inset of (b): Photograph of a film with increasing P/Cu ratio from bottom left to top right. When the P/Cu ratio decreases below roughly 1, the appearance of the film changes from dark red (characteristic of metallic Cu₃P) to grey (characteristic of metallic Cu₃P). (c): Reflective index and extinction coefficient of the same CuP₂₀ film shown in (b).
properties may be influenced by inhomogeneity, as exemplified by the dual-phase morphology shown in Fig. 4. Nevertheless, important qualitative trends in the transport properties of these films as a function of composition can still be discerned.

The temperature dependence of the electrical conductivity (Fig. 7(a)) suggests that CuP$_{2-y}$ is a nondegenerate doped semiconductor and that the two other films are either metallic or degenerately doped semiconductors. Hall effect measurements at room temperature confirm this interpretation (Fig. 8), with high carrier concentrations measured in Cu$_{3-z}$P and Cu$_{1.61}$P (above $10^{20}$ cm$^{-3}$) and a moderate carrier concentration measured in CuP$_{2-y}$ ($10^{15}$ cm$^{-3}$–$10^{17}$ cm$^{-3}$). All films have a positive Hall voltage confirming their $p$-type conductivity. Note that the conductivity of Cu$_{1.61}$P and CuP$_{2-y}$ after one month of storage is appreciably lower (Fig. 7(a)), highlighting possible stability issues as discussed in the previous sections.

Due to the inverse relationship between carrier concentration and thermovoltage, the Seebeck coefficient is highest in CuP$_{2-y}$ and lowest in Cu$_3$P (Fig. 7(b)). Interestingly, the Seebeck coefficient increases linearly with temperature in all three films (Fig. 7(b)). This behavior is often a sign of a temperature-independent carrier concentration, a typical feature of materials with non-zero density of states at the Fermi level (i.e., metals and degenerate semiconductors such as Cu$_{3-z}$P and Cu$_{1.61}$P). However, a linear increase of the Seebeck coefficient with temperature is not readily explained for a more weakly doped semiconductor like CuP$_{2-y}$. In an ideal scenario, we would expect the carrier concentration to increase with temperature due to increasing defect ionization, and the Seebeck coefficient to decrease accordingly. The reason for this discrepancy is unclear. One could invoke the role of film inhomogeneity due to the presence of Cu$_3$P secondary phases (Fig. 4), or assume that the increase of electrical conductivity with temperature (Fig. 7(a)) is due to mobility changes rather than to the hole concentration changes. Yet, a simultaneous increase in hole concentration and Seebeck coefficient with temperature was reported for CuP$_2$ single crystals, where inhomogeneity effects can be excluded. Multi-band transport could also cause an unusual temperature behavior due to increasing contributions from the additional valence band pockets of CuP$_2$ with increasing temperature. However, application of the Boltzmann transport equation on the calculated CuP$_2$ band structure reveals that a significant decrease in the Seebeck coefficient is expected in the 200 K–300 K range assuming a concurrent increase in hole concentration by one order of magnitude (Fig. S6, Supporting Information).

As another hypothesis, one could assume that CuP$_{2-y}$ is highly compensated by donor defects at low temperatures, but its $p$-type character becomes more dominant at higher temperatures due to activation of a deeper acceptor. If this hypothesis is correct, one would expect both the electrical conductivity and the Seebeck coefficient to increase with temperature as we experimentally observe – the former due to an increase in the concentration of ionized acceptors, the latter due to a decreasing contribution from the (negative) $n$-type Seebeck coefficient. Previous work also suggested the possibility of charge compensation in CuP$_2$ single crystals based on the temperature dependence of their carrier mobility. The position of the acceptor level in our CuP$_{2-y}$ film can be estimated as (121 ± 3) meV above the valence band from an Arrhenius plot of the electrical conductivity in the 230 K–300 K temperature range (Fig. S7, Supporting Information).

The room-temperature thermal conductivity of CuP$_{2-y}$ is 1.1 W/Km (Fig. 7(c)). This value is lower than in CuP$_2$ single crystals (3.6 W/Km–4.7 W/Km depending on lattice direction) as may be expected for a polycrystalline sample. Our measured conductivity is, however, in excellent agreement with the calculated 1.12 W/Km amorphous limit for bulk CuP$_2$. The
increasing thermal conductivity with increasing temperature is unlike the \( 1/T \) behavior typical of crystalline semiconductors in this temperature range. Instead, it is often observed in amorphous or highly disordered materials, consistently with the observation that our measured conductivity is very close to the amorphous limit. Based on these results, we assume that the phonon mean free path in the CuP\(_2-y\) film is low due to disorder\(^{40}\) and/or phonon boundary scattering.\(^{41}\) The latter is likely enhanced by the small grains, low thickness, and porous morphology of the film.\(^{40–42}\) The electronic contribution to the thermal conductivity is negligible due to the low hole concentration of CuP\(_2-y\) (Fig. 8). The thermal conductivities of Cu\(_3-y\)P and Cu\(_{1.61}\)P are only slightly higher and their temperature dependences are similar to the case of CuP\(_2-y\). Thus, we conclude that the thermal conductivity is phonon-mediated and strongly limited by film morphology in all three films. In fact, scattering of charge carriers (holes) is also morphology-limited. The hole mobility of the present Cu\(_3-y\)P film \((0.27 \text{ cm}^2/\text{Vs})\) is two orders of magnitude lower than in a continuous CuP film on glass with about the same carrier concentration \((28.8 \text{ cm}^2/\text{Vs})\), see Fig. 8).

CuP\(_2\) has recently been proposed as a potential thermoelectric material.\(^{12,13}\) Our measurements on a CuP\(_2-y\) film confirm that the lattice contribution to its thermal conductivity is indeed sufficiently low for thermoelectric applications. However, the thermoelectric figure of merit \(zT\) at room temperature is still low for all investigated compositions (Fig 7(d)) due to low power factors (Fig S8, Supporting Information). In the vicinity of the Cu\(_3\)P stoichiometry, the main issue is a low Seebeck coefficient. In the vicinity of the CuP\(_2\) stoichiometry, the main issue is low electrical conductivity. Even taking the more favorable properties of our CuP\(_2\) films on glass (Table I) or of previously reported CuP\(_2\) single crystals\(^8\) the \(zT\) value at room temperature would only be 0.004 and 0.05, respectively. It might be possible to optimize the hole concentration of CuP\(_2\) by extrinsic doping to obtain higher \(zT\) values. Nevertheless, phosphorus losses at moderate temperatures and potential stability issues under ambient conditions are likely to limit its practical applicability in thermoelectric devices. Similar issues might exist in other phosphorus-rich phosphides.

### III. CONCLUSION

We deposited amorphous CuP\(_{2+x}\) thin films with a wide range of \(x\) (positive and negative) by reactive sputtering in a PH\(_3/\text{Ar}\) atmosphere. Either a metallic Cu target or a compound Cu\(_3\)P target can be used as a deposition source. Some of the amorphous CuP\(_{2+x}\) films could be converted to polycrystalline CuP\(_2\) by rapid thermal annealing in an inert atmosphere at 1 bar. Three conditions must be satisfied to do so: (i) short annealing times, (ii) moderate annealing temperatures in the 350°C–450°C range, and (iii) initial composition sufficiently close to the ideal CuP\(_2\) stoichiometry. Remarkably, amorphous films that were either too P-poor or too P-rich quickly decomposed into CuP\(_3\) and gaseous phosphorus upon heating. This “compositional lock-in” behavior highlights the importance of pre-existing short-range order for kinetic stabilization of materials under conditions where decomposition and crystallization are in competition with each other.

Polycrystalline CuP\(_{2+x}\) films are semiconductors with native p-type conductivity. Their electrical properties are rather insensitive to elemental composition in the vicinity of the stoichiometric point, and only moderately affected by the annealing conditions. The thermal conductivity of a P-poor CuP\(_2\) film is 1.1 W/Km at room temperature, confirming its potential applicability as a thermoelectric material. However, the hole conductivity of CuP\(_2\) is too low to achieve a high power factor (and therefore a high \(zT\) value) without extrinsic doping. Furthermore, decomposition of CuP\(_2\) into Cu\(_3\)P and gaseous phosphorus at around 400°C hinders high-temperature applications. Although stability issues are not mentioned in the CuP\(_2\) single-crystal literature, our polycrystalline CuP\(_{2+x}\) films were only stable in ambient conditions for a few days. It is currently not clear if this issue is related to the porous morphology of our films, or if it is an

| TABLE I. List of electrical, optical, and thermal properties measured in this study on post-annealed CuP\(_{2+x}\) films at room temperature. The film composition is CuP\(_{2.0}\) for all properties except for the thermal conductivity (CuP\(_{1.35}\)). |
|---------------------------------|---------|----------|
| **Electrical conductivity**    | 0.5–1.0 | S/cm     |
| **Seebeck coefficient**        | +390 ± 10 | µV/K    |
| **Thermal conductivity**       | 1.1 ± 0.1 | W/Km    |
| **Band gap**                   | 1.5 ± 0.1 | eV      |
| **Work function**              | 5.0 ± 0.1 | eV      |
| **Dielectric constant** (\(\varepsilon_\infty\)) | 10.5 ± 1.0 |        |
intrinsinc behavior of CuP$_2$.

Finally, CuP$_2$ is a stronger light absorber than many established photovoltaic materials, with absorption coefficient rapidly rising to $10^5$ cm$^{-1}$ above its 1.5 eV band gap. Combined with a native doping density in the optimal range for a photovoltaic absorber in a pn junction solar cell ($10^{15}$ cm$^{-3}$–$10^{17}$ cm$^{-3}$), we conclude that CuP$_2$ may deserve more detailed optoelectronic characterization.

IV. EXPERIMENTAL DETAILS

A. Film growth

Amorphous CuP$_{2+x}$ thin films were deposited on Corning Eagle XG borosilicate glass by reactive radiofrequency (RF) sputtering over a $10 \times 5$ cm$^2$ area. A Cu target and a Cu$_3$P target were co-sputtered at 2 Pa total pressure in a PH$_3$/Ar atmosphere without intentional heating and without substrate rotation. The targets were oriented so that one short side of the substrate would mainly be coated by the Cu target and the other short side by the Cu$_3$P target.

Immediately after deposition, CuP$_{2+x}$ films were cut into smaller pieces and annealed in a lamp-based rapid thermal annealing (RTA) furnace in a N$_2$ atmosphere. Because of the sputtering target geometry and differences in their applied power, small gradients in P/Cu ratio and film thickness were obtained across the substrate. These gradients enabled us to characterize several data points (“samples”) for each annealing run, each with a distinct composition and thickness. More details on film deposition and annealing are available in the Supporting Information.

B. Film characterization

All measurements except for nanocalorimetry and thermoelectric/Hall effect characterization were performed within 24 h after annealing to avoid sample degradation. The combinatorial characterization data arising from compositional gradients in the films was managed with the COMBIgor tool, and integrated into the High-Throughput Experimental Materials Database.

Elemental composition and film thickness were determined by x-ray fluorescence (XRF) calibrated by Rutherford backscattering spectrometry (RBS, composition) and spectroscopic ellipsometry (thickness). X-ray diffraction (XRD) measurements were conducted using Cu K$_\alpha$ radiation, a 2D detector, and a fixed incidence angle of 10$^\circ$. Raman spectra were measured with 532 nm excitation wavelength and 4 W/mm$^2$ power density. Scanning electron microscopy (SEM) images were taken at 5 kV beam voltage.

Sheet resistance was measured with a collinear four-point probe directly contacting the film. The Seebeck coefficient of a CuP$_2$ film on glass was measured in a custom-built setup using In contacts. The work function was measured with a Kelvin probe calibrated with a standard Au sample. Absorption coefficient and optical functions were extracted by spectroscopic ellipsometry. Due to higher porosity in the upper part of the film, we modeled the system as a glass substrate of known optical functions, a CuP$_2$ layer with a linearly increasing fraction of air from bottom to top, and a roughness layer treated with Bruggeman effective medium theory.

For nanocalorimetry and thermoelectric/Hall effect characterization, CuP$_{2+x}$ films were deposited on previously described microfabricated chips designed for calorimetry and in-plane thermoelectric characterization of thin-film samples. In both types of chips, CuP$_{2+x}$ was deposited on a free-standing Si$_3$N$_4$ membrane. Due to the fragility of the membrane, thinner CuP$_{2+x}$ films (90 nm–120 nm) were employed for these studies.

Nanocalorimetry experiments were conducted in a N$_2$ atmosphere on an as-deposited amorphous film with initial CuP$_{2.5}$ composition, with an average heating rate of roughly 5000 °C/s. Temperature-dependent thermoelectric characterization (electrical and thermal conductivity and Seebeck coefficient) was performed in vacuum on three films with different compositions after annealing. The electrical conductivity was measured using the van der Pauw (vdP) method. The Seebeck coefficient was measured with respect to platinum metals lines using an internal four-probe platinum thermometer. The thermal conductivity was derived from the current-voltage characteristics of membrane heaters/thermometers in the self-heating regime. The hole concentration and mobility were measured on the same samples by double AC Hall. More details on all measurements are available in the Supporting Information.

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endorsement by the National Institute of Standards and Technology (NIST), nor does it imply that the products identified are necessarily the best available for the purpose. Nanocalorimeter fabrication was performed in part at the NIST Center for Nanoscale Science & Technology (CNST).

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SUPPORTING INFORMATION

EXTENDED EXPERIMENTAL DETAILS

Film growth

Amorphous CuP$_{2+x}$ thin films were deposited on Corning Eagle XG borosilicate glass by reactive radio-frequency (RF) sputtering over a 10 × 5 cm$^2$ area in a PVD Products sputter system with base pressure in the 10$^{-6}$ Pa range. A Cu target and a Cu$_2$P target (both 2" diameter, 0.25" thickness, 99.99% purity) were co-sputtered at 2 Pa total pressure in a PH$_3$/Ar atmosphere without intentional heating and without substrate rotation. To obtain a CuP$_{2.5}$ composition, we employed 5% PH$_3$ in Ar, a total flow rate of 0.028 L/min, and RF sputter powers of 15 W (Cu$_2$P) and 10 W (Cu). The target-substrate distance was 16 cm and the deposition rate was about 0.2 Å s$^{-1}$. To obtain a lower P content, we decreased the PH$_3$ concentration at constant total pressure. To obtain a higher P content, we decreased the RF powers on both targets by the same proportion. The targets were oriented so that one short side of the substrate would mainly be coated by the Cu target and the other short side by the Cu$_2$P target. The P/Cu ratio of the film varied by about 10% across the long direction (10 cm long), confirming that the surfaces of both targets are in a similar phosphorus-enriched state, giving comparable deposition rates. Depositing CuP$_2$ at lower sputter pressures would require higher PH$_3$ concentrations which were not available in our setup. At 2 Pa sputter pressure, it was not possible to crystallize CuP$_2$ directly during sputter deposition by increasing the substrate temperature, due to severe P re-evaporation from the film. Substantially higher sputter pressures might prevent re-evaporation, but at the likely expense of deposition rate and film quality.

Immediately after deposition, CuP$_{2+x}$ films were cut into smaller pieces and annealed in a lamp-based rapid thermal annealing (RTA) furnace (MILA-3000, ADVANCE RIKO, Inc.). The samples were placed on a Si susceptor in a quartz tube, the furnace was closed, purged with N$_2$ for 5 min, and the desired annealing steps were executed under an N$_2$ flow at 1 bar. For all processes discussed in the articles, the temperature was held at 150 °C for 1 min and then ramped up to the desired annealing temperature at 3 °C/s. The temperature was controlled through a feedback loop by monitoring the temperature of the Si susceptor. After annealing, the furnace was actively cooled with water and the samples were taken out at room temperature.

Characterization of films deposited on glass

All measurements except for nanocalorimetry and thermoelectric/Hall effect characterization were performed within 24 h after annealing to avoid sample degradation. Elemental composition and film thickness were determined by x-ray fluorescence (XRF) in a Bruker Tornado M4 instrument at 2 × 10$^3$ Pa pressure using a Rh source. XRF spectra were fitted with the Bruker XMethod analysis program. The composition was calibrated by Rutherford backscattering spectroscopy (RBS) measurements of separate CuP$_{2+x}$ films of different thicknesses and compositions deposited on Si (Fig. S9). The thickness was calibrated by spectroscopic ellipsometry measurements of the same films (see below). RBS was performed using a model 3S-MR10 RBS system from National Electrostatics Corporation in a 168° backscattering configuration, using a 2 MeV He$^+$ beam. Samples were measured until the total integrated charge delivered to the sample was 80 μC, and signals were added together when multiple measurements were taken at a single point. Film composition from RBS was determined by fitting using the RUMP analysis software.\(^1\)

X-ray diffraction (XRD) measurements were conducted with a Bruker D8 diffractometer using Cu K$_\alpha$ radiation, a 2D detector, and a fixed incidence angle of 10$^\circ$. The diffraction intensity at each 2θ angle was integrated over the χ range measured by the 2D detector. Raman spectra were measured with a Renishaw inVia Raman microscope under laser light excitation at 532 nm wavelength and 4 W/mm$^2$ power density. Scanning electron microscopy (SEM) images were taken with a Hitachi S-3400N instrument with a field emission gun and 5 kV beam voltage.

Sheet resistance was measured with a collinear four-point probe directly contacting the film, and electrical conductivity was derived from it using the XRF-determined thickness. The Seebeck coefficient of a CuP$_2$ film on glass was measured in a custom-built setup using In contacts and four temperature differences in the vicinity of room temperature. The work function was measured with a SKP SPV LE 450 Kelvin probe (KP Technology) calibrated with a standard Au sample.

Absorption coefficient and optical functions were extracted by spectroscopic ellipsometry using a J.A. Woollam M-2000 rotating-compensator ellipsometer and three incidence angles. Due to higher porosity in the upper part of the film, we modeled the system as a glass substrate of known optical functions, a CuP$_2$ layer with a linearly increasing fraction of air from bottom to top,\(^2\) and a roughness layer treated with Bruggeman effective medium theory. The
optical functions of CuP\textsubscript{2} were represented by a Kramers-Kronig-consistent b-spline function with 0.1 nodes/eV. Ellipsometry spectra were fitted with the CompleteEase software (J.A. Woollam).

Nanocalorimetry and thermoelectric characterization of films deposited on Si\textsubscript{3}N\textsubscript{4} membranes

For nanocalorimetry and thermoelectric/Hall effect characterization, CuP\textsubscript{2+x} films were deposited on previously described microfabricated chips designed for calorimetry\textsuperscript{4} and in-plane thermoelectric characterization\textsuperscript{4} of thin-film samples. In both types of chips, CuP\textsubscript{2+x} was deposited on a free-standing Si\textsubscript{3}N\textsubscript{4} membrane. Due to the fragility of the membrane, thinner CuP\textsubscript{2+x} films (90 nm–120 nm) were employed for these studies. Since these samples had to be shipped for measurements, they were packed in vacuum after their last processing step and unpacked just before the measurement. Both calorimetry and thermoelectric measurements took place about a month after the samples had been packed.

Nanocalorimetry experiments were conducted in a N\textsubscript{2} atmosphere on an as-deposited amorphous film with initial CuP\textsubscript{2,5} composition. The film was heated to about 510\(^\circ\)C for a duration of 100 ms and the average heating rate is roughly 5000\(^\circ\)C/s. The heat released in the 300\(^\circ\)C–400\(^\circ\)C range was estimated as the area under the assumed heat capacity baseline divided by the volume of the film and the atomic density of CuP\textsubscript{2} in the P\textsubscript{21}/c structure (0.062 atoms/Å\textsuperscript{3}).

Temperature-dependent thermoelectric characterization (electrical and thermal conductivity and Seebeck coefficient) was performed in vacuum on three films annealed under different conditions (composition before annealing: CuP\textsubscript{2,5}). We found that phosphorus losses in CuP\textsubscript{2+x} films deposited on the chips for thermoelectric characterization were much faster than in the films deposited on glass. Two possible reasons are the lower thickness and better thermal contact with the Si susceptor. A Cu\textsubscript{15}P\textsubscript{50} film (labeled “Cu\textsubscript{2−}P\textsuperscript{x}”) was obtained by annealing at 400\(^\circ\)C for 30 s. A Cu\textsubscript{16}P\textsubscript{35} film was obtained by annealing at 350\(^\circ\)C for 5 min. A Cu\textsubscript{13}P\textsubscript{35} film (labeled “CuP\textsubscript{2−}y”) was obtained by annealing at 350\(^\circ\)C for 30 s. Before thermoelectric characterization, the chips were glued to ceramic 24 pin dual-in-line (DIL) chip packages using silver epoxy and wire bonded with aluminum wires. The packages were characterized in a tailored closed cycle refrigerator (Janis), providing vacuum down to \( p = 7 \times 10^{-7} \text{mbar}, \) coaxial wiring to the packages, triple temperature shielding and a temperature range from 10 K–500 K. The setup and analysis routines were verified by reference measurements on 100 nm gold films.

The electrical conductivity of the Cu-P films was measured by current-voltage (I-V) lines\textsuperscript{4} using the van der Pauw (vdP) method\textsuperscript{4} and excitation currents of 100 µA (Cu\textsubscript{3−}P) and 1 µA (Cu\textsubscript{1}P and CuP\textsubscript{2−}y). The I-V characteristics show linear behavior (see Fig. S10(a–c)) for the shown data range in Fig. 7(a) of the main article. Some of the low-temperature data was discarded due to a noisy vdP correction factor in Cu\textsubscript{1}P and high contact resistances (> \( 1 \times 10^{8} \Omega \)) in CuP\textsubscript{2−}y, resulting in non-linear I-V characteristics.

For temperature-dependent Seebeck coefficient measurements, the Seebeck voltage \( V_{S}(I_{\text{heat}}, T) \) and the resistance of the nearby four-probe platinum thermometer \( R_{P}(I_{\text{heat}}, T) \) were measured as function of different heating currents \( I_{\text{heat}} \) at bath temperature \( T \).\textsuperscript{4} The chip’s individual thermometer calibration is given by \( R_{P}(I_{\text{heat}} = 0, T) \). Using this calibration, \( V_{S} \) (low potential on the cold side) can be expressed as function of the temperature difference \( \Delta T_{S} \).

For all samples \( V_{S} \) was proportional to \( I_{\text{heat}}^{2} \) and \( \Delta T_{S} \), as expected and shown in Fig. S10(d–f). The relative Seebeck coefficient with respect to the platinum metals lines was found as \( S_{\text{Cu-P}} = S_{\text{Cu-P}} - S_{\text{Pt}} = -\partial V_{S}/\partial \Delta T_{S} \). For calculation of the absolute Seebeck coefficient \( S_{\text{Cu-P}} \), reference data of Kockert \textit{et al.} was used (sample PT3).\textsuperscript{8} Some of the low-temperature data in Fig. 7(b) of the main article was discarded due to increasing contact resistance that hindered accurate voltage measurements.

For determination of the films thermal conductivity, the I-V characteristics of both membrane heaters were measured with high resolution and with \( I_{\text{sh}} \) in the self-heating regime.\textsuperscript{4} Here, the membrane heaters act as thermometers at the same time. Using the local derivative, the resistance \( R_{\text{sh}} \) can be expressed as function of the applied power \( P_{\text{sh}} \).

\( R_{\text{sh}}(P_{\text{sh}}) \) shows a linear relation as expected. The intercept of the linear regression of \( R_{\text{sh}}(P_{\text{sh}}) \) yield the individual thermometer calibration for both membranes. Using this calibration and considering that \( \partial V/\partial I = R(P_{\text{sh}} = 0) + 3\Delta R_{\text{sh}} \) the resistance change \( R_{\text{sh}}(P_{\text{sh}}) \) can be converted to \( \Delta T_{\text{sh}}(P_{\text{sh}}) \) for both membranes. Linear regression yield the thermal resistance \( \partial P_{\text{sh}}/\partial \Delta T_{\text{sh}} \) for the large and the small membrane (Fig. S10(g–i)). Application of the math given in Völklein \textit{et al.}\textsuperscript{6} and measurements of the empty membrane result in the thermal conductivity of the film.

After thermoelectric characterization, the DIL packages were connected to the room temperature sample holder of a 8404 Hall measurement system (LakeShore). Using two MFLI lock-in amplifiers (Zurich Instruments AG) and a CS580 voltage driven current source (Stanford Research Systems) the double AC Hall (DAC) method\textsuperscript{7} was applied to significantly increase the signal to noise ratio. Our setup is verified by DC reference measurements on InAs. Here, the frequency of the magnetic field \( f_{B} = 0.8 \text{ Hz} \) and the frequency of the current excitation was set to \( f_{I} = 77 \text{ Hz} \). For different excitation currents \( I_{\text{ex}} \) and different magnetic field \( B \) up to 0.3 T the Hall voltage \( V_{H} = V(f_{I} + F_{H}) + V(f_{I} - F_{H}) \) was measured. The linear relationship of \( V_{H}(I_{\text{ex}} \cdot B) \) proves the Hall effect as origin and allows the determination
of the carrier density. The error bars in Fig. 8 of the main article are derived from the standard error of the linear fits of $V_H$ versus ($I_{ex} \cdot B$) plots for each sample.

SUPPLEMENTARY FIGURES

FIG. S1. EDX point spectra on a post-annealed film with overall CuP$_{1.3}$ composition. The intensity ratio between the Cu L line and the P K line increases by a factor $\sim 5.5$ when moving from the darker matrix to the brighter islands. Thus, we conclude that the matrix consists of CuP$_2$ and the islands consist of Cu$_3$P.

FIG. S2. XRD patterns of CuP$_{2+x}$ films annealed under different conditions. All films have CuP$_{2.0}$ composition after annealing, except for the film labeled as “P-poor”, which has CuP$_{1.6}$ composition. Reference reflections for CuP$_2$ in the P2$_1$/c structure$^9$ and for Cu$_3$P in the P6$_3$cm structure$^{10}$ are shown. The asterisks indicate Bragg reflections attributed to Cu$_3$P.
FIG. S3. Thermovoltage measurements on a CuP$_{2.0}$ film on glass after annealing. The absolute Seebeck coefficient ($S_{\text{CuP}_2}$) of CuP$_{2.0}$ is extracted as the slope of the fitted line with reverse sign, plus the known Seebeck coefficient of the In contacts used for the measurement, following the convention $S_{\text{CuP}_2,\text{In}} = S_{\text{CuP}_2} - S_{\text{In}} = -\partial V_s/\partial \Delta T$.

FIG. S4. Electrical conductivity of post-annealed CuP$_{2+x}$ films as a function of annealing conditions and final composition. The data is the same as in Fig. 6(a) of the main article, but here the focus is on the data points close to the P/Cu = 2 composition.
FIG. S5. Real ($\varepsilon_1$) and imaginary part ($\varepsilon_2$) of the dielectric function of a CuP$_{2.0}$ film on glass after annealing. The spectra are derived from the ellipsometry-determined refractive index and extinction coefficient shown in Fig. 6(c) of the main article.

FIG. S6. Calculated Seebeck coefficient of CuP$_2$ as a function of temperature. The Seebeck coefficient is determined by semiclassical Boltzmann transport theory using the BoltzTraP2 package$^{11}$ on the CuP$_2$ band structure. We employed the band structure calculated by density functional theory under the generalized gradient approximation (GGA) and available on the Materials Project database (mp-927).$^{12}$ The p-type Seebeck coefficient is calculated at different hole concentrations, indicated by colors. A hole relaxation time of 10 fs is assumed. We further assume that the increase in conductivity of the experimental CuP$_{2-y}$ sample with temperature (Fig. 7(a), main article) is due to increasing hole concentration, which is in the $10^{15}$ cm$^{-3}$ range at room temperature (Fig. 8, main article). Under these assumptions, the arrow from $1 \times 10^{16}$ cm$^{-3}$ at 200 K to $9 \times 10^{16}$ cm$^{-3}$ at 300 K roughly indicates the expected temperature dependence of the Seebeck coefficient for a p-type CuP$_2$ crystal. The transport calculations include the possible influence of other valence band maxima energetically close to the absolute valence band maximum along the $\Gamma$–Y line.
FIG. S7. Arrhenius plot of the electrical resistivity of a post-annealed CuP$_{2-y}$ film deposited on a Si$_3$N$_4$ membrane. An activation energy of (121 ± 3) meV can be extracted for the mechanism responsible for the conductivity increase above 230 K.

FIG. S8. Temperature-dependent power factor $\sigma S^2$ of the three films used for thermoelectric characterization. $\sigma$ is the electrical conductivity and $S$ is the Seebeck coefficient.
FIG. S9. Examples of RBS spectra of Cu-P films used to calibrate composition measurements by XRF. For each sample, we show the fitted stoichiometric coefficients of Cu and P.
FIG. S10. Processed raw data for thermoelectric characterization is shown for Cu$_{3-x}$P, Cu$_{1.6}$P and CuP$_{2-y}$. (a-c) Linear behavior of I-V curves at different temperatures are shown. (d-f) The measured Seebeck voltage as function of the temperature difference is shown along with the extracted slope characterizing the relative Seebeck coefficient of the films with respect to platinum, with opposite sign. (g-i) Temperature increase of the membrane line heaters is shown as function of the applied power. Thermal resistances shown in red and blue result from the linear regression.
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