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Supplementary information

Synthesis and properties of copper nitride, a metastable semiconductor

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Supplementary information

Copper nitride thin films were prepared by radio-frequency (RF) reactive magnetron sputtering of a 50 mm circular copper target in an argon and nitrogen atmosphere. Power supplied to the target was 15, 20, or 25 W, and the depositions were carried out with the target fully poisoned. A 50 mm by 50 mm glass substrate was cleaned in an ultrasonic bath, first with acetone and second with isopropanol. The substrate was then subjected to oxygen plasma to remove any organic residue. This substrate was mounted in the deposition chamber at an angle of 45° relative to the sputter gun. The near side of the sample was 13 cm from the gun and the far side of the sample was 15 cm from the gun. The top side of the substrate was mounted with silver paste to a heater set to 250 °C, and the remainder of the substrate was suspended in vacuum. This produced a temperature gradient perpendicular to the target-substrate distance (d_{TS}) gradient, such that each point on the substrate experienced different growth conditions. The temperature at the substrate surface varied from 280 °C (slightly above the set point) to 140 °C. Prior to deposition, the target was preconditioned by sputtering for at least 30 minutes with a shutter in front of the substrate.

The flow rate of both nitrogen and argon was 10 sccm, and the total chamber pressure was 20 mTorr. The argon was supplied through a mass flow controller and the nitrogen was supplied through an atomic gas source (Oxford Applied Research model HD25) and controlled by a calibrated needle valve. The atomic gas source is designed to crack gas molecules using a radio-frequency field, and was turned on to produce some of the samples and kept off for others. When the atomic gas source was on, the power was set to 250 W. After a 3.5 hour deposition, the sample was allowed to cool with argon and nitrogen flowing and the sputter gun and atomic gas source off, and it was then removed from the chamber.

As shown in Fig. S1a, using an atomic nitrogen source significantly improves the phase purity and preferential orientation of Cu_3N thin films. In contrast, changing the power applied to the copper target with the nitrogen atom source in operation does not appreciably influence the phase purity and 00L orientation of the resulting Cu_3N thin films, under otherwise equal deposition conditions (Fig. S1b). Together, these two results indicate that the high activity of nitrogen is a more important component for growth of phase-pure Cu_3N thin films than the rate at which these thin films are synthesized, within the range of investigated synthesis conditions.

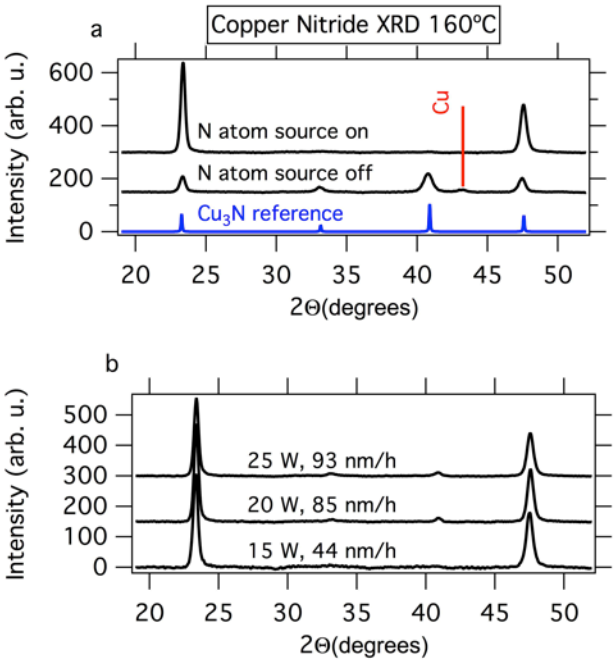

Fig. S1 (a) XRD patterns of films grown at 20 W Cu, 160 °C, and d_{TS} = 13 cm with the cracker on at 250 W (on) and 0 W (off). (b) XRD patterns of films grown at 160 °C, and d_{TS} = 13.8 cm with the cracker on at 250 W. All XRD patterns are normalized for film thickness and diffraction collection time.

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Both structural and optical properties changed as a function of target-substrate distance. Shown in Figure S2 is an alternative representation of Figure 3 from the main text.

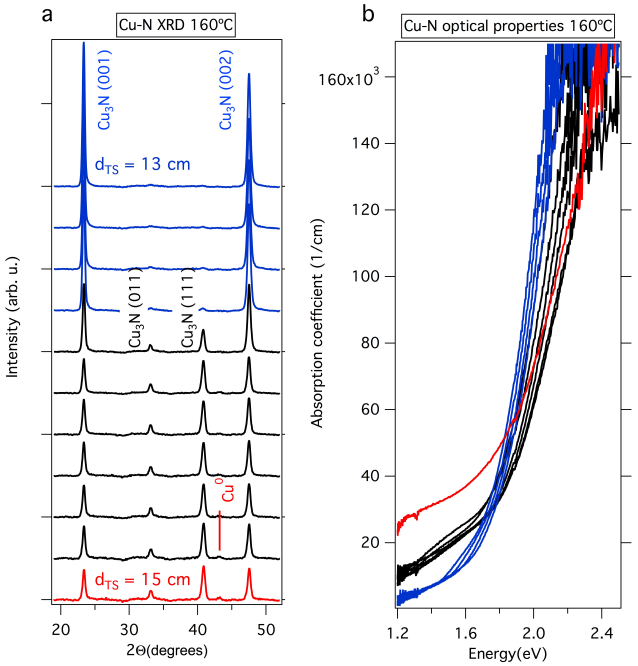

Fig. S1 (a) XRD patterns of films grown at 20 W Cu, 160 °C, and d_{TS} ranging from 13 cm (top blue trace) to 15 cm (red trace). (b) Optical characterization of the same films.

Analysis of our results from copper nitride indicate that binary nitride compounds with $\Delta H_f = +1$eV/N should be accessible by the method of sputtering with an atomic nitrogen source. This motivated the synthetic study of three other metastable nitrides of tin, antimony and bismuth. Tin nitride adopts the spinel crystal structure and has Sn_3N_4 chemical composition. No crystallographic information or chemical composition is available in literature or databases for either bismuth nitride or antimony nitride. Shown in Figure S3 are XRD patterns of the results of sputtering these metals in a nitrogen and argon atmosphere. The top trace in each pane is the lowest temperature at which metallic precipitates were observed in XRD at a target-substrate distance of 13 cm.

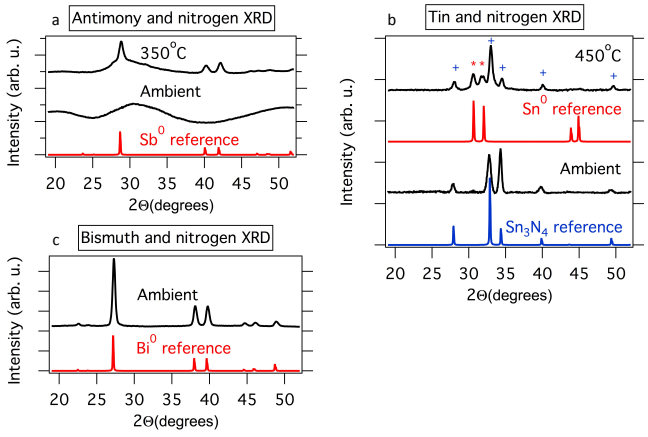

Fig. S3: XRD patterns of films obtained by sputtering (a) antimony, (b) tin, and (c) bismuth in a nitrogen and argon atmosphere with an atomic nitrogen source. In the top pattern of (b) metallic tin is marked by (*) while tin nitride is marked with (+).