Devices for Thermal Conductivity Measurements of Electroplated Bi for X-ray TES Absorbers

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Abstract
Electroplated bismuth (Bi) is commonly used in transition-edge sensors (TESs) for X-rays because of its high stopping power and low heat capacity (Collan in Phys Rev B 1:2888, 1970, Yan in Appl Phys Lett 111:192602, 2017). Electroplated Bi is usually grown on top of another metal that acts as seed layer, typically gold (Au), making it challenging to extrapolate its thermoelectric properties. In this work, we present four-wire resistance measurement structures that allow us to measure resistance as a function of temperature of electroplated Bi independently of Au. The results show that the thermal conductivity of the Bi at 3 K is high enough to ensure the correct thermalization of X-ray photons when used as an absorber for TESs.

Keywords Bismuth · Transition-edge sensors · Resistivity · Thermal conductivity · Cryogenic · X-ray

1 Introduction

Transition-edge sensors (TESs) are seeing increasing use in synchrotron X-ray facilities. Their energy resolution, 10–100× better than comparable silicon-drift diode sensors, enables new science in the areas of X-ray emission spectroscopy [3], Compton scattering [4], and XAFS [5]. One of the challenges in developing X-ray TESs is to fabricate a suitable absorber with sufficient X-ray stopping power (energies in the 6–100 keV range) while also retaining good thermalization properties to avoid position-dependent responses and keeping the total heat capacity limited to retain high-energy resolution. Gold (Au) and bismuth (Bi) form a common combination that works because both have good stopping power, where Au is characterized by

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very high thermal conductivity [6] even at cryogenic temperatures, and Bi has lower heat capacity [1] due to its limited number of carriers. At the same time, this could affect the thermal conductivity of the material at cryogenic temperatures, negatively affecting the performance of the sensor.

The resistivity (\(\rho\)) is a common proxy for describing thermal properties of materials at lower temperatures. Previous work has estimated a lower \(\rho\) for electroplated Bi compared to thermally evaporated Bi [7]. However, the presence of an electrically conductive Au seed layer underneath an electroplated Bi film poses a difficulty for directly measuring \(\rho\). In this paper, we describe the deployment of a four-wire resistance measurement structure fabricated to isolate the Bi contribution and thus allow a more direct measurement of its electrothermal properties at cryogenic temperatures.

2 Device Design and Fabrication

2.1 Device Design

The electroplating of Bi is usually obtained by electrochemically growing the Bi on top of a seed layer. This is convenient because for X-ray TESs, Bi is always coupled with another absorbing material, typically Au. If the four-wire measurement structure was to be fabricated directly on the stack of Bi and Au, \(\rho\) measurements would be dominated by the higher conductivity of the Au layer [6]. Some precautions could be taken to minimize the effect, like using thinner Au layers and tuning the Bi electroplating conditions to maximize its conductivity [8], but ultimately the convolution of the two contributions would be measured.

To measure the electroplated Bi resistivity independently from the underlaying Au layer, the devices represented in the SEM image in Fig. 1 have been fabricated. The inset of Fig. 1 is a 3D rendering of the same device zoomed in on the area

![Fig. 1](image-url)
between the voltage leads. The devices are composed of four separate leads patterned in a Au-thin film, which also acts as a seed layer for the electrochemical growth of the Bi. During the electrochemical deposition, the Bi grows initially on top of the Au seed layer. The growth is somewhat isotropic, unless otherwise constricted. In these devices, a thick photoresist mold is present, which directs the growth of the Bi mainly vertically out of the plane of the wafer and subsequently parallel to the wafer plane, in the direction that connects the four leads. When enough material has been deposited, the Bi grown from each lead eventually meets in the middle of the mold, forming a continuous micro-wire of Bi, which represents the only element of electrical continuity between the Au leads. Therefore, the voltage drop between the two inner leads is determined only by the Bi resistance. Structures of several dimensions have been fabricated to study the limits of this approach and to check that the measured resistances would scale with the device lateral dimensions. A length of 100 µm between the voltage leads represented the maximum that could be achieved reliably. Devices of three different widths have been fabricated at this length: 20, 50 and 100 µm. All the devices were fabricated on a SiO₂/Si wafer to minimize current leakage through the wafer at all temperatures.

2.2 Device Fabrication

Au was used as the conductive seed layer for plating Bi and formed the measurement pads for the four-wire resistance measurement structures. 100 nm Au with a 5 nm Ti adhesion layer was deposited by sputtering and patterned by liftoff (lithography via Heidelberg MLA150). A ~ 23 µm layer of AZ P4620 photoresist formed the Bi plating mold. This required a two-layer spin process; longer, cooler soft-bake cycles; and multiple exposures in the MLA150 to prevent bubbling in the photoresist. The wafer was prepared for plating with a 1-min O₂ plasma RIE descum and a 10-s dip in dilute nitric acid for surface wetting. The electrolyte consisted of bismuth-nitrate pentahydrate dissolved in a mixture of nitric acid, glycerol, and tartaric acid, buffered with KOH to a pH of ~0.15. (Process was adapted from [9].) For this electrolyte, maintaining a pH below ~0.3 is required to prevent Bi precipitates. However, plating is inhibited if pH falls close to 0. The electrolyte pH may be adjusted simply by adding either nitric acid or KOH, as required. Plating was completed in the beaker-suspended version of the “Beaker on a Stick” wafer plating holder from Wafer Power Technologies [10]. Wafers were plated at room temperature, and the solution was not agitated [8]. Plating required a low-throw process; the current density for these wafers was 7.7 mA/cm². A given wafer was plated for 60 min, at which time the Bi thickness was estimated via profilometry, measuring the difference between the photoresist mold of known thickness and the surface of the Bi film. The plating rate was estimated to be ~220–250 nm/min in the larger Bi structures. The wafer was then plated an additional 90–120 min to allow enough lateral growth for the Bi to form a bridge between the Au fingers.

The wafer was rinsed in dilute nitric acid to prevent Bi precipitates on the plated surface, followed by DI water. A protective layer of AZ P4620 covered the Bi
structures for dicing. Chips were diced, and photoresist was removed by acetone and isopropyl alcohol before measurement.

3 Results and Discussion

The resistance ($R$) of Bi micro-wires of various dimensions has been measured as a function of temperature ($T$) from 300 to 3 K. In Table 1 are reported the measured resistance values at 300 K for devices of the same length ($l$) but of different width ($w$) averaged over several samples. All the devices have a thickness of approximately 30 µm. For reference, the expected resistance for each type of device, based on the resistivity for bulk Bi, is also reported [6].

The averaged measured resistance at 300 K closely matches the expected resistance from bulk resistivity [6]. The devices whose resistance differs the most from the expected value are the 100 × 20 variant. This is probably due to the difficulty in properly defining the actual device dimensions due to the large grain size of Bi in the micro-wire, grains being several µm wide. The close match between expected and measured resistance provides confidence in the validity of the structure for the measurement of electroplated Bi resistance.

Figure 2 shows two $\rho$ vs $T$ curves (cold colors—bottom and left axes) for a 20 µm (circles) and a 100 µm (triangles) device, respectively, measured from 300 K down to 3 K. The trends are similar for both devices. The resistivity initially falls approximately linearly with temperature down until about 230 K. Below this temperature, the resistivity starts to rise all the way down to approximately 25 K, at which point it saturates. The rise in resistivity resembles that of a semiconductor, but this is not the entire story. The first sign against a simple semiconductive nature of the micro-wire is the fact that the resistivity saturates at low temperature, instead of diverging as it should in the presence of an energy gap in the carrier density of states. One possible explanation for the saturation effect is the activation of some form of extra conduction channels at lower temperatures, which has been hypothesized in Bi crystals [11]. The second sign against the semiconductive nature of the device is the non-exponential rise in resistance. The warm-colored curves in Fig. 2 show the natural logarithm of the resistivity as a function of the inverse of temperature (top and right axes); the curves show only a marginally linear dependence in the range ~ 25–65 K. Conversely, a non-exponential rise of the resistivity with lowering temperatures can

| $l \times w$ (µm x µm) | Bulk $R$ @ 300 K (Ω) | Device $R$ @ 300 K(Ω) | $\kappa$ @ 3 K (W*m⁻¹*K⁻¹) |
|------------------------|----------------------|------------------------|-----------------------------|
| 100 × 20               | 0.198                | 0.190                  | 4.62 × 10⁻²                 |
| 100 × 50               | 0.086                | 0.086                  | 3.47 × 10⁻²                 |
| 100 × 100              | 0.041                | 0.042                  | 3.44 × 10⁻²                 |

Expected resistance at 300 K from bulk resistivity [6] is also reported. All devices are approximately 30 µm thick ($t$).
be explained in terms of the temperature dependence of the overlapping valence and conduction bands in a semimetal [11]. Similar trends in the resistivity versus temperature have been seen in Bi crystals under pressure [11]. Finally, the curves show also sizable jumps in resistivity, present in all the measured devices.

Another interesting consideration is the mechanics of the polycrystalline Bi film and its interaction with the substrate. Bi has a coefficient of thermal expansion several times higher than Si [12], a mismatch between device and substrate that could lead to mechanical stress when devices are cooled. Deformation of the unit cell of Bi is known to affect the conduction properties of the material [11]. Further studies are needed to understand these phenomena.

Knowledge of the low-temperature resistivity of the micro-wire allows us to estimate the thermal conductivity at cold. The thermal conductivity ($\kappa$) in metals is proportional to the electrical conductivity ($\sigma$) through the Lorenz number ($L$), as stated by the phenomenological law of Wiedemann–Franz

$$\kappa = \sigma L T$$

The Lorenz number is a material-dependent number. We derived an estimate for our devices by using $\kappa$ and $\rho$ for bulk Bi at 300 K from the literature [6]. The approach is justified by the good agreement between the measured electrical resistivity and the resistivity for bulk, as shown in Table 1. The resulting $\kappa$ at base temperature is reported in Table 1.

The Bi micro-wire devices have an average $\kappa$ about 2 orders of magnitude lower than that of the Au film used as seed layer and absorbers in our sensors ($\sim 7.8$ Wm$^{-1}$ K$^{-1}$). This is expected given the semimetal nature of Bi. At the same time, the thermal conductivity of the SiN membranes in our TESs ($\sim 1.2 \times 10^{-5}$ Wm$^{-1}$ K$^{-1}$—estimated from the current–voltage) is about 3 orders of magnitude lower than that of these test devices, which represents a lower limit for intrinsic $\kappa$ of the Bi electroplated in a TES. This ensures that the heat generated by the absorption of an X-ray
photon in the Au/Bi absorber stack will thermalize within the TESs before escaping to the thermal bath through the SiN membrane if the thermal connection between the TES and the absorber is higher than all the other thermal conductances involved (typical in real devices).

4 Conclusions

In this work, we described the fabrication of test structures for measuring thermoelectric properties of electroplated materials while eliminating the contribution from the underlying seed layer. We showed that the electroplated Bi typically used as an X-ray absorber in TESs has an acceptable thermal conductance at operational temperatures, ensuring that even at the high thicknesses needed for absorption of high-energy photons, no position-dependence effect should take place.

Future work could focus on studying Bi electrical properties at cold for different growth conditions, as well as the effect of the mechanical stress induced by differential contraction between the substrate and the Bi. Such studies may inform future TES absorber fabrication.

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Data Availability

The data that support the findings of this study are available on request from the corresponding author OQ.

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