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# Tuning the crystallinity of thermoelectric Bi<sub>2</sub>Te<sub>3</sub> nanowire arrays grown by pulsed electrodeposition

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# Abstract

Arrays of thermoelectric bismuth telluride (Bi<sub>2</sub>Te<sub>3</sub>) nanowires were grown into porous anodic alumina (PAA) membranes prepared by a two-step anodization. Bi<sub>2</sub>Te<sub>3</sub> nanowire arrays were deposited by galvanostatic, potentiostatic and pulsed electrodeposition from aqueous solution at room temperature. Depending on the electrodeposition method and as a consequence of different growth mechanisms, Bi<sub>2</sub>Te<sub>3</sub> nanowires exhibit different types of crystalline microstructure. Bi<sub>2</sub>Te<sub>3</sub> nanowire arrays, especially those grown by pulsed electrodeposition, have a highly oriented crystalline structure and were grown uniformly as compared to those grown by other electrodeposition techniques used. X-ray diffraction (XRD) analyses are indicative of the existence of a preferred growth orientation. High resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) confirm the formation of a preferred orientation and highly crystalline structure of the grown nanowires. The nanowires were further analyzed by scanning electron microscopy (SEM). Energy dispersive x-ray spectrometry (EDX) indicates that the composition of Bi-Te nanowires can be controlled by the electrodeposition method and the relaxation time in the pulsed electrodeposition approach. The samples fabricated by pulsed electrodeposition were electrically characterized within the temperature range 240 K  $\leq T \leq$  470 K. Below  $T \approx$  440 K, the nanowire arrays exhibited a semiconducting behavior. Depending on the relaxation time in the pulsed electrodeposition, the semiconductor energy gaps were estimated to be 210-290 meV. At higher temperatures, as a consequence of the enhanced carrier-phonon scattering, the measured electrical resistances increased slightly. The Seebeck coefficient was measured for every Bi<sub>2</sub>Te<sub>3</sub> sample at room temperature by a very simple method. All samples showed a positive value  $(12-33 \ \mu V \ K^{-1})$ , indicating a p-type semiconductor behavior.

(Some figures in this article are in colour only in the electronic version)

# 1. Introduction

The fabrication of nanowire arrays has attracted an increasing interest. Low-dimensional thermoelectric materials have a higher figure of merit (FOM) due to quantum confinement effects caused by the change in the density of electronic states (DOS) as a function of material dimension as well as the increase of phonon scattering [1]. Consequently, potential applications to thermoelectric devices have been explored. Theoretical investigations have suggested that

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low-dimensional materials may exhibit FOM values considerably larger than 1.0 [1, 2].

Many candidate thermoelectric materials have been investigated, such as Bi,  $Bi_{1-x}Sb_x$ ,  $Bi_{2-x}Sb_xTe_3$ , and  $Bi_2Te_{3-y}Se_y$ . Thin films grown by various techniques have been reported previously [3–5]. Similarly, nanowire arrays fabricated by various techniques have been reported, too [6–9]. Among these various thermoelectric materials, bismuth telluride ( $Bi_2Te_3$ ) and its derivative compounds are very attractive candidates for thermoelectric applications near room temperature [10–14].

Many syntheses for the preparation of thermoelectric materials have been reported previously, such as pressure injection [15], vapor-phase deposition [16, 17], metal organic chemical vapor deposition [18, 19], hot wall epitaxy [20], sputtering [21], and cyclic electrodeposition [22]. Among the templated approaches, electrodeposition is one of the most popular techniques to fabricate nanowires of metals and intermetallic compounds [23]. It offers the advantages of cost efficiency, rapid deposition rate, relatively easy tuning ability of the nanowire stoichiometry, and uniform growth [10]. Up to now, three different electrodeposition techniques have been applied to the fabrication of Bi2Te3 nanowire arrays, namely galvanostatic [12], potentiostatic [11] and pulsed electrodeposition [24]. In particular, pulsed electrodeposition offers the advantage of uniform growth of Bi<sub>2</sub>Te<sub>3</sub> nanowires. This homogeneous growth of Bi<sub>2</sub>Te<sub>3</sub> nanowires by pulsed electrodeposition is influenced by the break (off) time of the pulsed electrodeposition. Additionally, this method is especially suitable for homogeneous deposition into high aspect ratio nanopores [25, 26].

In this paper, we report the fabrication of  $Bi_2Te_3$ nanowires grown by electrodeposition, mainly by pulsed electrodeposition, into a porous anodic alumina (PAA) membrane detached from the aluminum substrate. We investigate the crystalline structure of the  $Bi_2Te_3$  nanowires grown with different relaxation (break) times. After the fabrication of  $Bi_2Te_3$  nanowires, we measured the electrical resistance as a function of temperature of  $Bi_2Te_3$  nanowires grown by pulsed electrodeposition and the Seebeck coefficient of  $Bi_2Te_3$  nanowires grown by the different electrochemical deposition methods.

#### 2. Experimental details

Cyclic voltammetry (CV) was employed in preliminary experiments to find an optimum potential for the deposition of  $Bi_2Te_3$  nanowires with potentiostatic and potential pulsed electrodeposition. A Au layer was prepared by galvanostatic plating onto a silver plate (purity 99.9%) for CV measurement. The operating potential was between -0.9 and 0.9 V and the scan rate was 20 mV s<sup>-1</sup>.

The PAA was prepared by using a two-step anodization process in 0.3 M oxalic acid, as described previously [27]. After the second anodization, the anodization voltage was slowly reduced to 0.01 V to achieve effective elimination of the barrier layer (barrier layer thinning) and detachment of the PAA from the underlying aluminum substrate [28].

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All of the electrodepositions were carried out at room temperature. The Au layer was coated by conventional sputtering onto the top of the PAA. In addition, the Au electrode (ca 3–5  $\mu$ m) as a working electrode in the top of PAA was subsequently galvanostatically deposited from a Au electrodeposition solution under a cathodic current density of 1 mA cm<sup>-2</sup> onto the sputtered Au layer. All of the electrodeposition processes were performed in a PAR model 263A potentiostat/galvanostat with a threeelectrode configuration, in which a Pt wire was used as a counter electrode and Ag/AgCl/KCl(saturated) as a reference electrode. Bi ions provided from 0.021 M Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and 0.03 M HTeO<sub>2</sub><sup>+</sup> ions from Te powder (purity 99.999%) were dissolved in 2.75 M HNO<sub>3</sub>, and the pH of the electrolyte was adjusted to less than 1 (0.8–0.9) with HNO<sub>3</sub>. The  $Bi_2Te_3$ nanowires were grown by galvanostatic electrodeposition under a cathodic constant current density of 2.5 mA cm<sup>-2</sup> (abbreviated gal), by potentiostatic electrodeposition at an applied potential of +60 mV (abbreviated pot) and by potential pulsed electrodeposition at +60 mV with pulse time 5 ms and off-time (0 V) 10 ms, 20 ms, 30 ms, and 50 ms, respectively (abbreviated pu 10, pu 20, pu 30, and pu 50).

X-ray diffractometry (XRD, Philips with Cu K $\alpha$  radiation,  $\lambda = 1.5406$  Å) was employed to assess the crystalline structure of the Bi2Te3 nanowire arrays after removing the Au layer in an Au etching solution (KI<sub>3</sub>). Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), and selected area electron diffraction (SAED) were also used to determine the crystalline structure of the nanowire arrays. The PAA matrix and the Au electrode layer were dissolved in 2 M NaOH solution and the Au etching solution, respectively, and nanowires were rinsed with deionized (DI) water several times before TEM observation. A droplet of solution was placed on a carbon grid and allowed to dry at room temperature. Scanning electron microscopy (SEM, JSM 6340F) was used to determine the morphology of the Bi<sub>2</sub>Te<sub>3</sub> nanowires. An energy dispersive x-ray spectrometer (EDX) attached to the scanning electron microscope was used to investigate the composition of the Bi<sub>2</sub>Te<sub>3</sub> nanowire arrays. The electrical resistance was measured as a function of temperature (213–468 K) under 1  $\mu$ A current provided by a Keithley power source meter. The overfilled Bi2Te3 layer on the top surface of PAA was eliminated by mechanical polishing. Electrical contacts were defined by Au sputtering using a mask of 1 mm holder. Subsequently, two copper wires were glued with carbon conductive paste on both sides of the PAA and the electrical resistance of Bi2Te3 nanowires was measured in the two-point configuration. For the measurement of the Seebeck coefficient of Bi2Te3 nanowires, this consists in two pieces of copper whose temperatures are controlled with a Peltier effect element, one side hot and the other cold. The samples were placed in between for 10 min in order to obtain stabilization of their temperature gradient (15 K). Upon the thermal gradient application, voltage was created on the multimeter.

Current density (mA/cm<sup>2</sup>

-0.014

-1.0



02 04 06 08

**Figure 1.** Cyclic voltammetry (CV) of a Au working electrode deposited by electrochemical deposition on a silver plate in 0.021 M  $Bi(NO_3)_3 \cdot 5H_2O$ , 0.03 M  $HTeO_2^+$  and 2.757 M HNO\_3 solution in the operating voltage between -900 and +900 mV. (Scan rate: 20 mV s<sup>-1</sup>, surface area: 1.13 cm<sup>2</sup>, reference electrode: Ag/AgCl/KCl(saturated).)

potential (V)

0.8 0.6 0.4 0.2 0.0

# 3. Results and discussion

Figure 1 shows the cyclic voltammogram of the  $Bi^{3+}/HTeO_2^+$ electrolyte between the operating potentials -0.9 and +0.9 V. The aim of cyclic voltammetry (CV) is to determine an optimized potential for potentiostatic and potential pulsed electrodeposition as well as to investigate the behavior of  $Bi^{3+}$  and  $HTeO_2^+$  ions in preventing codeposition [29]. Two reduction peaks (labeled as peak A and peak B) were observed in the cathodic scan at +350 and -11 mV. Peak A is attributed to the reduction of  $HTeO_2^+$  and  $Bi^{3+}$  to  $Bi_2Te_3$  according to the following reaction:

$$3\text{HTeO}_2^+ + 2\text{Bi}^{3+} + 18\text{e}^- + 9\text{H}^+ \rightarrow \text{Bi}_2\text{Te}_3(s) + 6\text{H}_2\text{O}.$$

We assume that the direct deposition of Bi<sub>2</sub>Te<sub>3</sub> occurred instead of the codeposition of Bi(s) and Te(s) because of the negative Gibbs free energy of formation of Bi<sub>2</sub>Te<sub>3</sub> ( $\Delta G_0^{\rm f} =$ -899.088 kJ mol<sup>-1</sup>). The reduction peak B is attributed to the formation of Bi<sub>2</sub>Te<sub>3</sub> via an intermediate step according to the following reactions [29]:

$$\begin{split} \text{HTeO}_2^+ + 5\text{H}^+ + 6\text{e}^- &\rightarrow \text{H}_2\text{Te} + 2\text{H}_2\text{O} \text{ (intermediate)} \\ \\ 3\text{H}_2\text{Te} + 2\text{Bi}^{3+} &\rightarrow \text{Bi}_2\text{Te}_3 + 6\text{H}^+. \end{split}$$

There is another reduction part at the potential of less than -600 mV, which is due to the onset of hydrogen evolution. When a more negative voltage (-600 mV) was applied, the Bi<sub>2</sub>Te<sub>3</sub> film on the silver plate floated after electrodeposition due to poor adhesion caused by vigorous hydrogen evolution in the electrolyte. The optimized reduction potential was determined as +60 mV, allowing the continuous growth of Bi<sub>2</sub>Te<sub>3</sub> nanowires for potentiostatic as well as for pulsed potential electrodeposition [30, 31].

Figure 2(a) shows the schematic structure of  $Bi_2Te_3$ nanowires growth in the PAA.  $Bi_2Te_3$  nanowires were grown from the Au layer in the PAA by galvanostatic, potentiostatic and pulsed electrodeposition. Inhomogeneous nanowire growth was observed in the galvanostatic and potentiostatic electrodeposition methods. Figures 2(b)–(d) show the cross-sectional scanning electron micrographs of  $Bi_2Te_3$ nanowire arrays grown with different types of electrochemical



**Figure 2.** Schematic of  $Bi_2Te_3$  nanowire growth ( $\Delta h$  describes an inhomogeneous  $Bi_2Te_3$  nanowire growth in the galvanostatic and potentiostatic methods) in the free standing PAA (a), cross-section of  $Bi_2Te_3$  nanowire arrays grown by the different electrochemical deposition methods, respectively. ((b): galvanostatic (2.5 mA cm<sup>-2</sup>), (c): potentiostatic (+60 mV), (d): pulsed electrodeposition (off-time: 30 ms).)

Table 1. Harris texture coefficients of various Bi<sub>2</sub>Te<sub>3</sub> nanowire arrays grown under different electrodeposition methods.

| Sample     |                                 | gal (2.5 mA cm <sup>-2</sup> ) | pot (+60 mV) | pu 10 | pu 20 | pu 30 | pu 50 |
|------------|---------------------------------|--------------------------------|--------------|-------|-------|-------|-------|
| Texture co | oefficient, TC <sub>(hkl)</sub> | 0.77                           | 0.81         | 0.68  | 0.82  | 0.98  | 1.633 |

deposition. The inhomogeneity in the nanowire growth ( $\Delta h_{gal}$ and  $\Delta h_{pot}$ , as shown in figures 2(b) and (c)) reached about 45%. Pulsed electrodeposition is much more effective for the homogeneous growth of nanowires. This observation could be explained as follows: during electrodeposition, the concentration of metal ions at the cathode interfaces decreases with reaction time, but this problem can be improved in pulsed electrodeposition. This is because the relaxation time ( $t_{off}$ ) plays an important role in the recovery and redistribution of the metal ion concentration at the deposition interface during the off-time. In addition, the relaxation time limits the hydrogen evolution occurring at the surface of PAA during electrodeposition [25].

Figure 3 shows the XRD patterns of  $Bi_2Te_3$  nanowire arrays. First of all, no peaks were observed for elemental Bi and Te, indicating that only the  $Bi_2Te_3$  phase is present. The Au (111), (200) and (222) orientation peaks are detected due to imperfect removal of the Au electrode layer. One orientation, the (110) peak, dominates in all samples. It is evident that the  $Bi_2Te_3$  nanowire arrays have a highly preferred orientation peak along the [110] axes perpendicular to the bottom of the PAA. Prieto *et al* reported that  $Bi_2Te_3$  nanowire arrays grow preferentially in the [110] direction [31]. We used the Harris texture coefficient to describe the degree of preferred orientation quantitatively [32, 33]. The texture coefficient ( $TC_{(hkl)}$ ) is defined as

$$\mathrm{TC}_{(hkl)} = (I_{hkl}/I_{hkl}^{0}) \Big/ \Big[ (1/N) \sum \left( I_{hkl}/I_{hkl}^{0} \right) \Big],$$

where  $I_{hkl}$  and  $I_{hkl}^{0}$  are the relative diffraction intensities of the plane (*hkl*) in the experimental and standard reference (JCPDS, No. 15-0863), respectively. *N* is the number of reflection faces in the diffraction pattern. If the TC is larger than 1.0, it indicates that the (*hkl*) plane is a preferred orientation of the crystallites. Table 1 summarizes the texture coefficient value obtained for each sample for the (110) plane. As shown in table 1, the value of TC<sub>((110))</sub> is larger than 1.0 in the pu 50 sample. This result shows the (110) plane of the pu 50 sample to be a preferred orientation. The TCs of Bi<sub>2</sub>Te<sub>3</sub> nanowires grown by pulsed electrodeposition are relatively larger than of those grown by other electrodeposition techniques, indicating that pulsed electrodeposition is a more effective method to grow highly oriented crystalline Bi<sub>2</sub>Te<sub>3</sub> nanowire arrays into PAA.

Figure 4 shows typical TEM micrographs and the corresponding SAED patterns of our  $Bi_2Te_3$  nanowires. The diameter of the nanowires (40 nm) is equal to the pore size of the PAA templates. Figure 4(a) shows the polycrystalline structure of nanowires grown by the potentiostatic method (a similar image results from the galvanostatic method). The  $Bi_2Te_3$  nanowires grown by pulsed electrodeposition have an almost single crystalline structure, consistent with the



**Figure 3.** XRD patterns of the  $Bi_2Te_3$  nanowire arrays fabricated with different electrochemical deposition methods. (Gal: galvanostatic (2.5 mA cm<sup>-2</sup>), pot: potentiostatic (+60 mV), pu 10, 20, 30, and 50: pulsed electrodeposition with relaxation time 10, 20, 30, and 50 ms.)

XRD result. As comparison to pulsed electrodeposition with different relaxation time, the crystallinity of Bi<sub>2</sub>Te<sub>3</sub> nanowires is enhanced and it becomes a nearly single crystalline structure with increasing relaxation time. This phenomenon is attributed to recrystallization during the break time for pulsed electrodeposition [34]. The increased relaxation time results in grain growth due to recrystallization during sufficient off-time. The most plausible explanation is that the bigger grains are thermodynamically more stable: if sufficient time is allowed to the system, the most stable state will be reached [34]. The SAED patterns of pu 30 and 50 samples, especially, indicate the rhombohedral space group (a = 4.385 Å and c = 30.48 Å) and single crystalline structure. Typical HRTEM images of an individual Bi<sub>2</sub>Te<sub>3</sub> nanowire grown by pulsed



**Figure 4.** TEM micrographs and corresponding SAED patterns of  $Bi_2Te_3$  nanowires prepared by (a) potentiostatic, (b) pulsed electrodeposition with 10 ms (pu 10), (c) with 30 ms (pu 30), and with (d) 50 ms (pu 50) relaxation times, respectively.



Figure 5. HRTEM micrographs of single  $Bi_2Te_3$  nanowires prepared by pulsed electrodeposition with 30 ms ((a) and (c)), and 50 ms relaxation time ((b) and (d)).

electrodeposition with 30 and 50 ms relaxation times are shown in figure 5. Interplanar distances of about 0.322 and 0.219 nm are visible, consistent with the interplanar distances of the (015) and (110) planes, respectively, confirming the XRD data. In addition, [110] is the preferred orientation direction for pulsed electrodeposition with 50 ms relaxation time.



Figure 6. The correlation between the atomic ratio of Bi and Te and the Seebeck coefficient value in Bi–Te nanowire arrays grown by different electrodeposition methods. Open symbol (O): Seebeck coefficient and closed symbol ( $\bullet$ ): atomic ratio. (The Seebeck coefficient of 'pot' samples is not displayed because of our experimental failure.)

Figure 6 shows the correlation between compositional analysis of Bi-Te nanowires and the Seebeck coefficient value for samples grown under different electrochemical conditions. Since the measurements of the Seebeck coefficient are independent of the number of measured nanowires, these measurements are as informative as single nanowire measurements [35]. The atomic ratio of Bi to Te becomes stoichiometrically near to 2:3 as the relaxation time increases in the pulsed electrodeposition method, indicating that the composition could be controlled by relaxation time. Bi-Te nanowires grown under galvanostatic and pulsed electrodeposition with less than 20 ms relaxation time show a p-type (Bi-rich) behavior, which has an excess of holes from the valence band (the Seebeck coefficient of Bi-Te nanowires grown under potentiostatic electrodeposition is not displayed due to our experimental failure). Despite the lower value than that of bulk p-type Bi<sub>2</sub>Te<sub>3</sub>, the positive value of the Seebeck coefficient was consistent with p-type semiconductor characteristics, too. Other previously published results gave Seebeck coefficient values of 270  $\mu$ V K<sup>-1</sup>, even film 81  $\mu$ V K<sup>-1</sup> [36, 37]. Our lower value was attributed to unoptimized doping concentration, which automatically leads to a low carrier concentration. The Bi-Te nanowires grown under galvanostatic and pulsed electrodeposition with less than 20 ms relaxation time showed relatively higher Seebeck coefficient values (ca 30  $\mu$ V K<sup>-1</sup>), most likely due to an increased hole concentration caused by the Bi-rich composition of the nanowires.

Figure 7(a) shows the measured electrical resistance of  $Bi_2Te_3$  nanowire arrays as a function of temperature. As the temperature falls, the sample resistances increase. This is a typical semiconducting behavior. However, the resistance enhancement at lower temperatures can be due to two distinct mechanisms, i.e., deactivation of the charge carriers of impurity levels, and/or the reduction of the intrinsic charge carriers in the specimen. To investigate these possibilities in more detail, assuming a  $R = R_0 \exp(E_a/2k_BT)$  dependence for the resistance, we have made numerical fits to the measured data. Here,  $R_0$  is the asymptotic value of the electrical

resistance at higher temperatures,  $E_a$  is the impurity activation energy or the energy gap of the semiconductor, and  $k_{\rm B}$  is the Boltzmann constant. The obtained values for  $E_a$  are 287 meV, 276 meV, 243 meV, and 215 meV for the pu 50, pu 30, pu 20, and pu 10 samples, respectively. Comparing these values to the energy gap of bulk semiconducting Bi2Te3 at room temperature, 145 meV [38], and to the corresponding thermal energies,  $k_{\rm B}T \sim 25$  meV, we conclude that  $E_{\rm a}$  should correspond to a semiconducting energy gap. The fact that the extracted value for the gap is larger than that of the bulk state is in accordance with the expectation that, as the sample size shrinks, the energy gap becomes larger. To exclude the possible existence of artificial effects, we have also measured the current-voltage (I-V) characteristics of the samples at different temperatures. Figure 7(b) shows the results of such a measurement. The I-V curves are linear up to the highest temperatures and down to the smallest bias currents. These observations confirm the formation of good ohmic contacts to the embedded nanowires. Instead, figure 7(c) displays an enlarged view of the resistance-temperature characteristic at higher temperatures. From  $T \approx 440$  K upward, except for the pu 10 sample, the resistances increase. We believe that this is a signature of the enhanced carrier-phonon scattering at higher temperatures.

Due to the large uncertainties in the number of electrically contacted nanowires in the membrane, N, determination of the electrical resistivity  $\rho$  of a single nanowire is not reliable. For an array of about 15  $\mu$ m long, 40 nm thick wires grown in an alumina template with a 110 nm pore periodicity, one arrives at a ratio  $\rho/N \sim 10^{-5} \Omega$  m. As the total number of nanowires over a 1 mm<sup>2</sup> area is about  $3 \times 10^8$ , and assuming that the electrical resistivity of nanowires is not very much different from the bulk value,  $\rho \sim 10^{-5} \Omega$  m [37], the fraction of electrically contacted wires can be estimated to be as low as  $1:10^8$ . Unambiguous values for the resistivity, as well as for certain other transport properties, can only be reliably obtained by performing measurements on individual nanowires. We are currently working on this matter.

# 4. Conclusions

Thermoelectric Bi2Te3 nanowires were successfully fabricated in well ordered PAA prepared by a two-step anodization process. Galvanostatic, potentiostatic and pulsed electrodeposition methods for the fabrication of nanowire arrays were compared. Pulsed electrodeposition is the most effective method to develop a homogeneous and highly crystalline structure of the Bi<sub>2</sub>Te<sub>3</sub> nanowires. Additionally, sufficiently long relaxation times allow for high crystallinity due to their grain growth attributed to the recrystallization. Therefore, Bi2Te3 nanowires grown with relatively long relaxation times between deposition pulses, such as 30 and 50 ms, show a highly preferred orientation along the [110] directions and are close to being single crystalline. In the electrical measurement, Bi2Te3 nanowires fabricated with different relaxation times in pulsed electrodeposition showed a semiconducting behavior. The ratio of electrical resistivity to the number of electrically contacted nanowires over an area of 1 mm<sup>2</sup> was estimated to be



**Figure 7.** (a) Dependence of the electrical resistance, R, on temperature, T, for different samples. The solid lines are theoretical fits to the measured data (see text). (b) The current (I)-voltage (V) characteristic of the pu 30 sample at different temperatures. (c) The enlarged view of the R-T characteristic at higher temperatures. Note the linearity. The solid lines in the insets are guides to the eye.

 $\rho/N \sim 10^{-5} \ \Omega$  m. In the measurement of the Seebeck coefficient, Bi–Te nanowires grown under galvanostatic, potentiostatic and pulsed electrodeposition with less than 20 ms relaxation time showed relatively higher value (ca 30  $\mu V \ K^{-1}$ ) due to the increased carrier concentration.

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