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Large Seebeck coefficients and thermoelectric power factor of La-doped SrTiO₃ thin films

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Seebeck coefficients and conductivity of La-doped SrTiO₃ thin films grown by molecular beam epitaxy were measured as a function of carrier concentration. At low carrier concentrations, thin films show very high Seebeck coefficients (up to 980 μV K^{-1}). The maximum thermoelectric power factor was 39 μWcm^{-1} K^{-2} at a carrier concentration of 7×10^{20} cm^{-3}. La-delta-doped superlattices were also characterized and exhibited Seebeck coefficients of ~500 μV K^{-1}. The results are discussed in the context of reports of enhanced Seebeck coefficients in delta-doped SrTiO₃ superlattices. © *2010 American Institute of Physics.* [doi:10.1063/1.3471398]

The thermoelectric properties of SrTiO₃ have recently attracted renewed attention, because of its large thermopower (Seebeck coefficient).[1–6] The thermoelectric power factor of SrTiO₃ single crystals, defined as $S^2\sigma$, where S is the Seebeck coefficient and σ is the electrical conductivity, is as high as 36 μW/K^2 cm at room temperature,[2] which is comparable to that of commercial thermoelectrics.[2,7] The thermoelectric figure of merit, ZT, which is defined as $(S^2\sigma/\kappa)T$, where κ is the thermal conductivity and T the temperature, scales with the power factor. Therefore, SrTiO₃ could be promising for thermoelectric applications if its thermal conductivity can be reduced. Thin films allow for new approaches to enhance ZT by nanostructuring, including the growth of superlattices.[8–10] For example, Ohta and co-workers[11,12] investigated superlattices of thin (few unit cells) Nb-alloyed SrTiO₃ layers sandwiched between undoped SrTiO₃. A maximum Seebeck coefficient of -480 μV K^{-1} was reported. This value is higher than the bulk value at the same carrier concentration, assuming that all the carriers are confined in the doped layers.[11,12] Sandwiching thin Nb SrTiO₃ layers in an undoped SrTiO₃ matrix is similar to delta-doping and results in sub-band conduction having two-dimensional (2D) character.[13] However, it does not necessarily result in strong carrier confinement in the doped layer, particularly for the electrons in the highest occupied subbands and in materials with a large dielectric constant, such as SrTiO₃.[14]

We have recently shown that La-doped SrTiO₃ thin films grown by molecular beam epitaxy (MBE) exhibit low-temperature electron mobilities that exceed those of single crystals, which indicates that these films are of very high quality.[15] In this study, we investigate the room temperature Seebeck coefficients and the electrical conductivity of both uniformly and delta-doped SrTiO₃ thin films grown by MBE.

La-doped epitaxial SrTiO₃ films were grown by MBE on (001) SrTiO₃ and $(La_{0.3}Sr_{0.7})(Al_{0.65}Ta_{0.35})O_3$ (LSAT) single crystal substrates, respectively. Details of the growth process, the films' structural characteristics and low-temperature electron mobilities have been reported in detail elsewhere.[15–17] The film thicknesses were between 150 and 1500 nm. It is important to ensure oxygen stoichiometry and avoid sub-

strate conduction, which can lead to erroneous estimates of the three-dimensional (3D) carrier concentration (n_{3D}) from the measured 2D carrier concentration (n_{2D}).[18,19] Samples were oxygen annealed after growth and substrates were confirmed to be insulating. Furthermore, the carrier concentration in the films closely corresponded to the La-concentration, indicating that all La donors are ionized and donate one electron to the conduction band of SrTiO₃ over several orders of magnitude in doping concentration.[15] The delta-doped sample consisted of a 170 nm thick buffer layer of undoped SrTiO₃, followed by a ~3 nm thick La-doped SrTiO₃ layer, which was capped with 140 nm of undoped SrTiO₃. For the superlattices, delta-doped layers were separated by undoped SrTiO₃. The total thickness above the first delta-doped layer (140 nm) and the spacing between the delta-doped layers (15 nm) were kept constant for all samples. Ohmic contacts were Al/Ni/Au (40 nm/20 nm/150 nm) deposited by electron beam evaporation. Hall and resistance measurements were made either in Hall bar geometry with rectangular shaped samples (10×4 mm^2) or with square shaped samples in van der Pauw geometry. The sheet carrier concentration n_{2D} was calculated as $n_{2D} = 1/(e \times R_H)$ where R_H the measured 2D Hall coefficient and e the elemental charge. The room temperature Hall electron mobilities were nearly independent of carrier concentration and ranged from $6–9$ cm^{2}V^{-1}s^{-1}. For measurements of the Seebeck coefficient, Peltier modules were used to provide a temperature difference. At each temperature gradient, sufficient time was allowed for the temperature and voltage differences to stabilize. The potential difference was measured using an Agilent 34401A Digital Multimeter and plotted as a function of the temperature difference. The Seebeck coefficient was extracted from the slope of a linear fit. All Seebeck coefficients were negative, as expected for SrTiO₃.[1]

Figure 1(a) shows the room temperature Seebeck coefficients and electrical conductivity as a function of carrier concentration (n_{3D}) of films that are uniformly doped with La. All films are in the degenerately doped regime, even for relatively low carrier concentrations because of the high dielectric constant of SrTiO₃.[15] The largest value measured for the Seebeck coefficient in this study is about -980 μV K^{-1} at a carrier concentration of 4.8×10^{17} cm^{-3}. This compares well with the maximum Seebeck coefficient of reduced SrTiO₃ single crystals of -890 μV K^{-1} at a carrier concen-

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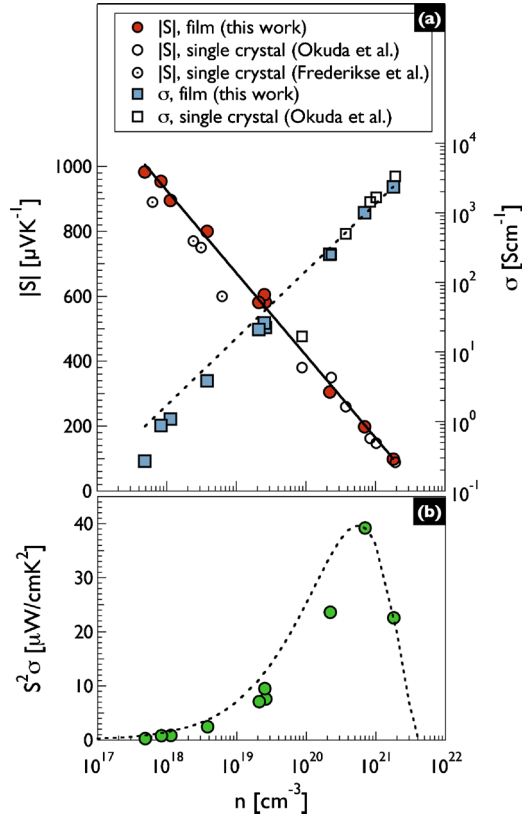
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FIG. 1. (Color online) (a) Magnitude of the Seebeck coefficient, $|S|$, (circles, left axis) and conductivity, σ, (squares, right axis) as a function of carrier concentration for the La-doped SrTiO$_3$ films in this study (filled symbols) and for single crystals in the literature (open symbols). The literature data is from Refs. 1 and 2. The solid line depicts the carrier concentration dependence of $|S|$ according to Eq. (1). The dashed line is a fit to the conductivity data. (b) The power factor of La-doped SrTiO$_3$ films, $S^2\sigma$, as a function of carrier concentration. The dashed line is the calculated power factor from the fits to the Seebeck coefficient and the conductivity data shown in (a).

TABLE I. Carrier concentrations and Seebeck coefficients for delta-doped superlattices as a function of the number x of delta-doped layers. The measured 2D (sheet) carrier concentration is n_{2D}. The 3D carrier concentration, which is derived from n_{2D}, is reported in two different ways, $n_{3D}^{(1)}$ and $n_{3D}^{(2)}$, where $n_{3D}^{(1)}$ is defined as n_{2D}/t and $n_{3D}^{(2)}$ as $n_{2D}/(x \times t_\delta)$.

x	$n_{2D}(\text{cm}^{-3})$	$n_{3D}^{(1)}(\text{cm}^{-3})$	$n_{3D}^{(2)}(\text{cm}^{-3})$	$|S|(\mu\text{V K}^{-1})$
1	9×10^{13}	3×10^{18}	3×10^{20}	548
4	2×10^{14}	6×10^{18}	2×10^{20}	500
8	6×10^{14}	2×10^{19}	3×10^{20}	480

show an inverse trend with carrier density. As expected [dashed line Fig. 1(b)] this results in a maximum of the power factor of the films of 39 μWcm^{-1} K^{-2} at a carrier concentration of 7×10^{20} cm^{-3} [Fig. 1(b)]. This is slightly larger than the maximum value reported for La-doped SrTiO$_3$ single crystals.[2] Assuming a thermal conductivity of $\sim$12 W/m K (Ref. 22) the estimated ZT at room temperature is $\sim$0.1. By developing approaches to reduce the thermal conductivity by about a factor of 6, ZT values similar to those of Bi$_2$Te$_3$,[7] a commercial thermoelectric, could be achieved at room temperature.

Table I shows the Seebeck coefficients of three delta-doped superlattices, where the number of delta-doped layers, x, was 1, 4, and 8, respectively. The Seebeck coefficients are about -500 μV K^{-1} and slightly decrease with the number of delta-doped layers. Table I also shows the 3D carrier concentrations calculated in two different ways for the three samples. One approximation assumes that $n_{3D}^{(1)} = n_{2D}/t$, where t is the total thickness of the entire grown structure (including the bottom and top undoped buffer and the spacer layers), i.e., as if the entire structure was uniformly doped. The second approximation, used in the prior literature,[11,12] assumes that all carriers are confined to the delta-doped layers, i.e., $n_{3D}^{(2)} = n_{2D}/(x \times t_\delta)$ where t_δ is the thickness of one delta-doped layer (3 nm). For the second approximation, it could be claimed that delta-doping enhances the Seebeck coefficient compared to bulk SrTiO$_3$ at a similar 3D carrier concentration ($\sim$ -300 μV K^{-1}). However, neither of the two approximations are correct for delta-doped layers, where the spatial extent of the wave function depends on the occupied subband index, causing the barriers to be conductive.[14] For example, even the surface of the $x=1$ sample, which is separated from the delta-doped layer by 140 nm of undoped SrTiO$_3$, was conductive, indicating that a significant fraction of carriers was not confined to the delta-doped layer. Thus the buffer layers are not insulating. A correct description of the power factor and Seebeck coefficient of the superlattice as a whole would require treating the barriers and the delta-doped layers as connected in parallel, which, however, requires knowledge of the transport properties (carrier concentrations and mobilities) of the individual layers.[9] Without this information, the results should not be used to claim a strong enhancement of the thermoelectric properties of the delta-doped superlattices.

In summary, we have shown that La-doped SrTiO$_3$ layers show Seebeck coefficients and thermoelectric power factors that are similar to those of single crystals with similar carrier concentration dependencies. Provided that the thermal conductivity can be reduced through nanostructuring, doped SrTiO$_3$ layers appear to be very promising for room temperature thermoelectric applications.

tration of 6×10^{17} cm^{-3}.[1] Further reduction in the carrier concentration would likely increase the Seebeck coefficient but not the power factor (see below). The decrease in the absolute value of the Seebeck coefficient with carrier concentration could be described by a simple expression, shown as a solid line in Fig. 1(a) as follows:

$$|S(\mu\text{V/K})| = 1180 - 254 \log\left(\frac{n_{3D}}{10^{17} \text{ cm}^{-3}}\right). \quad (1)$$

For nondegenerate semiconductors, the slope in Eq. (1) should be approximately $(k/e)\ln 10$, where k is the Boltzmann constant, or $\sim$200 μV/K.[7] Although a slightly different slope ($\sim$250 μV/K) is observed here, it is still within typical variations observed even for nondegenerate semiconductors.[20] For degenerate semiconductors, a carrier concentration dependent correction introduced by Fermi–Dirac statistics is needed[2,7] but appears to be constant over the range of carrier concentrations explored in Fig. 1(a). Furthermore, the conduction band structure of SrTiO$_3$ is complex, consisting of sixfold degenerate d-band states near the conduction band minimum.[21] For comparison, the Seebeck values of doped SrTiO$_3$ single crystals from Refs. 1 and 2 are also shown in Fig. 1(a). The Seebeck coefficients and their carrier concentration dependence are similar for the films and the single crystals, which attest to the high quality of the MBE grown films. The Seebeck coefficient and conductivity

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