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Dember effect induced photovoltage in perovskite *p*-*n* heterojunctions

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An unusual and rather large transient lateral photovoltage (LPV) has been observed in $La_{0.9}Sr_{0.1}MnO_3/SrNb_{0.01}Ti_{0.99}O_3$ and $La_{0.7}Sr_{0.3}MnO_3/Si$ heterojunctions under the nonuniform irradiation of pulsed laser. The irreversible LPVs on both sides of a *p*-*n* junction challenge the well established model for LPV in conventional semiconductor *p*-*n* junctions, which can be well explained by the Dember effect. Much larger LPV is observed in $La_{0.7}Sr_{0.3}MnO_3/Si$ than that in $La_{0.9}Sr_{0.1}MnO_3/SrNb_{0.01}Ti_{0.99}O_3$. Similar results measured from both substrates of $SrNb_{0.01}Ti_{0.99}O_3$ and Si also support such a Dember effect. Much larger LPVs in heterojunctions than those in simple samples ($SrNb_{0.01}Ti_{0.99}O_3$ or Si) suggest a potential application of Dember effect in heterostructures. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2772772]

One of the important characteristics of perovskite-based *p*-*n* junctions is the photoelectric effect.[1,2] Recently, we reported a lateral photovoltaic (LPV) effect measured on the surface of one side of the $La_{0.7}Sr_{0.3}MnO_3/Si$ heterojunctions, which can be explained by LPV theory for conventional semiconductor *p*-*n* junctions.[3] The LPV effect on conventional semiconducting *p*-*n* junction with nonuniform illumination was found 70 years ago and has been applied for use in position-sensitive detectors.[4–6] It is well known that sufficiently energetic radiation normally incident on a *p*-*n* junction produces a photovoltage across the junction. If the junction is nonuniformly irradiated, the photovoltage will vary with position, producing an additional photovoltage parallel to the plane of the junction, which was called LPV. The general understanding of the LPV for semiconductor *p*-*n* junction is that the optically generated hole-electron pairs cancel a portion of barrier space charge resulting in a lateral electric field which induces the lateral flow of majority carriers.[7,8] As the majority carriers in *p* side and that in *n* side are holes and electrons, respectively, the LPVs measured between two random positions on *p* side and those on *n* side are supposed to be reversed. In this letter, we will report an unusual transient LPV which is irreversible for both sides of $La_{0.9}Sr_{0.1}MnO_3/SNTO$ *p*-*n* junction and for both sides of $La_{0.7}Sr_{0.3}MnO_3/Si$ *p*-*n* junction. This phenomenon challenges the well established theory of LPV mentioned above for conventional semiconductors. A mechanism based on the difference between the mobilities of electrons and holes, i.e., Dember effect, is introduced to explain this phenomenon.

Dember effect was proposed 50 years ago to explain the light induced surface voltage (different from the bulk),[9] and the voltage caused in the two sides of a semiconductor sample due to the different mobility of light induced carriers. However, so far, there is not any Dember effect induced LPV phenomenon on *p*-*n* heterojunctions has been reported, as almost all previous reports only concentrated on the terahertz radiation generated by the Dember effect in simple semiconductor samples.[10–13]

$La_{0.9}Sr_{0.1}MnO_3/SNTO$ *p*-*n* junctions were fabricated by growing a *p*-type $La_{0.9}Sr_{0.1}MnO_3$ layer on *n*-type SNTO (001) substrates, following the procedure we reported previously.[2,14]

The schematic setup for LPV measurement is shown in the inset of Fig. 1. A small area of 0.5 mm diameter was irradiated on the *p*-$La_{0.9}Sr_{0.1}MnO_3$ surface by a 308 nm

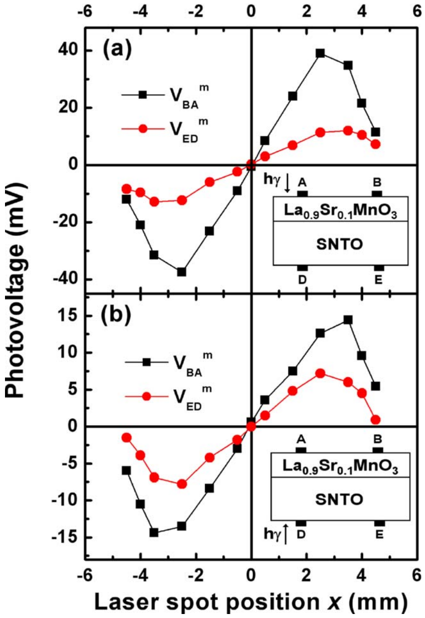

FIG. 1. (Color online) Peak LPVs V_{BA}^m and V_{ED}^m as a function of the position of the laser spot in the *x* direction for irradiating the $La_{0.9}Sr_{0.1}MnO_3/SNTO$ junction through (a) the $La_{0.9}Sr_{0.1}MnO_3$ side and (b) the SNTO side. The insets display the schematic setup for LPV measurement. *A* (−3 mm), *B* (3 mm), *D* (−3 mm), and *E* (3 mm) denote the electrodes.

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XeCl excimer laser beam (the pulse width of 20 ns, the irradiated energy of 0.15 mJ, and the repetition rate of one pulse every 5 min to avoid the heating effect). The LPV between the indium electrodes A ($x=-3$ mm) and B ($x=3$ mm) on the p-$La_{0.9}Sr_{0.1}MnO_3$ surface, V_{BA}, and that between the indium electrodes D ($x=-3$ mm) and E ($x=3$ mm) on n-SNTO surface, V_{ED}, were measured and recorded by a sampling oscilloscope of 500 MHz terminated into 1 MΩ at ambient temperature. Especially, the electrodes were always kept in the dark to prevent the generation of any electrical contact effect. The maximal LPV values, V_{BA}^m and V_{ED}^m of the transient signal are plotted in Fig. 1(a) as a function of the laser spot position (x) on the $La_{0.9}Sr_{0.1}MnO_3$ surface. It is clear that the transient LPV to laser pulse depends on the position of the laser spot in x axis and undergoes a sign reversal as the laser spot travels from one electrode to the other. The changeover in sign occurs at the middle (with $x=0$) of two electrodes.

For a more detailed investigation of LPV dependence on the laser spot position, the focus of laser was scanned along a pair of contacts on the p-$La_{0.9}Sr_{0.1}MnO_3$ side, A (−3 mm) and B (3 mm), and along those on the n-SNTO side, D (−3 mm) and E (3 mm), as shown in Fig. 1(a). When the light spot is at the center between A and B on the p-$La_{0.9}Sr_{0.1}MnO_3$, the lateral photovoltages V_{BA} and V_{ED} are zero due to the diffusion symmetry. If the light position x is positive (negative), V_{BA} (or V_{ED}) is positive (negative). Furthermore, the signal becomes stronger when the light spot is closer to B or A. From Fig. 1(a), we can see several significant characteristics of LPV: (i) the polarity reverses over the center point (with $x=0$); (ii) when the laser spot locates between the contacts, a monotonic increase of the absolute value occurs with the distances between the laser spot and the center position between the two contacts; (iii) maximum of the absolute value is obtained when the laser spot is very close to either one of the two contacts; (iv) moving the spot beyond the electrodes leads to a monotonous drop in the amplitude of LPV.

The well established theory for the LPV effect on conventional semiconductor p-n junction demonstrates that the region closer to the laser spot should be with higher electric potential in p side while the region closer to the laser spot should be with lower electric potential in n side, due to the laser induced majority carriers separated into p side and n side, respectively, by the built-in electric field in the charge region near the interface of p-n junction.[7] Based on this understanding, the sign of LPV measured on p side V_{BA}^m and the corresponding one measured on n side V_{ED}^m should be reversed for a p-n junction. However, from Fig. 1(a), we can clearly see that the sign of LPV measured on p side, V_{BA}^m, and the corresponding one measured on n side, V_{ED}^m, are the same (irreversible) for $La_{0.9}Sr_{0.1}MnO_3$/SNTO p-n junction.

It should be noticed that the above model of the laser induced majority carriers dominating LPV effect is only correct when the amount of laser induced carriers are small. In our experiment, the laser we used in the experiment is a 308 nm XeCl excimer laser beam with an energy density of 0.76 mJ/mm^2 in duration of 20 ns. In this case, the amount of laser induced carriers should be comparable with or even much larger than that of the majority carriers in the *oxide* semiconductor, so that both electrons and holes generated by phonons should play an important role in LPV. The reason causing the LPV in $La_{0.9}Sr_{0.1}MnO_3$/SNTO heterostructures is just the mobility difference between holes and electrons. The much larger mobility of electrons than that of holes makes the separation of electron-hole pairs, which results in a transient distribution of electrons far away from the laser spot and the holes staying closer to the spot. This transient distribution definitely causes a higher electric potential in the region closer to the laser spot, and this should be the intrinsic reason for the transient voltage in both sides of the p-n heterostructure. Based on this effect, we can understand our observed result that a monotonous increase of the absolute value of the LPV with the distance between the laser spot and the center position between the two contacts when the laser spot locates between the contacts. The larger the distance, the further the electrons go ahead of holes, and the larger the absolute value of the LPV measured. This is also why V_{BA} (or V_{ED}) is positive with laser spot being closer to B (or E) and V_{BA} (or V_{ED}) is negative with laser spot being closer to A (or D). Only this diffusion mechanism can explain the irreversible LPV phenomenon we observed. As both electrons and holes induced by photons exist on two sides of oxide p-n junctions, the mobility difference of electron and hole in diffusion from the laser spot point causes the same sign (positive or negative) of LPV on two sides of a p-n junction. The smaller amount of induced carriers on the n-SNTO side than that on p-$La_{0.9}Sr_{0.1}MnO_3$ side with the laser irradiating on p-$La_{0.9}Sr_{0.1}MnO_3$ surface causes the reduction of LPV measured on n-SNTO side than that of p-$La_{0.9}Sr_{0.1}MnO_3$ surface. It should be noted that only strong light can cause the Dember effect LPV to be observed. The 308 nm (≈4.03 eV) photon energy is above the band gap of $La_{0.9}Sr_{0.1}MnO_3$ (≈1.0 eV) and SNTO (≈3.2 eV), so that electron-hole pairs can be generated in both the p-$La_{0.9}Sr_{0.1}MnO_3$ layer and n-SNTO substrate (absorption measurement we took has proved that the laser can go through the $La_{0.9}Sr_{0.1}MnO_3$ film with an amplitude decay). Furthermore, the present results also indicate a rather large difference between mobility of electrons and that of holes in doped perovskite materials of the heterostructure.

To confirm the present mechanism dominating for the observed LPV, we made further measurement, let the laser irradiate the other side, i.e., the n-SNTO side, and observed the LPV, as shown in Fig. 1(b), which is exactly the same as what we expected based on the present understanding. For irradiating the p-$La_{0.9}Sr_{0.1}MnO_3$ surface, V_{ED}^m is reduced greatly compared with V_{BA}^m for $La_{0.9}Sr_{0.1}MnO_3$/SNTO junction, while there is less reduction of V_{ED}^m compared with V_{BA}^m in the case of irradiating the opposite surface of the junction, the n-SNTO surface. This different reduction of LPV for irradiating the different sides of junction can be easily understood in that more photon induced carriers in the substrate side (SNTO) are produced by laser irradiating on the substrate side than those by laser irradiating on the $La_{0.9}Sr_{0.1}MnO_3$ side, so that larger LPV caused by Dember effect is measured. From the results shown in Figs. 1(a) and 1(b), we can also find something beyond the Dember effect. The smaller V_{ED}^m than V_{BA}^m, in other words, larger LPV measured on p-type material than that on n-type one in the heterojunction, indicates that the well established mechanism for LPV in conventional semiconducting p-n junctions (majority dominating LPV) also plays a role in the LPV we observed on oxide p-n heterostructures. From the irreversible LPVs (V_{BA}^m or V_{ED}^m) (both being positive or both being nega-

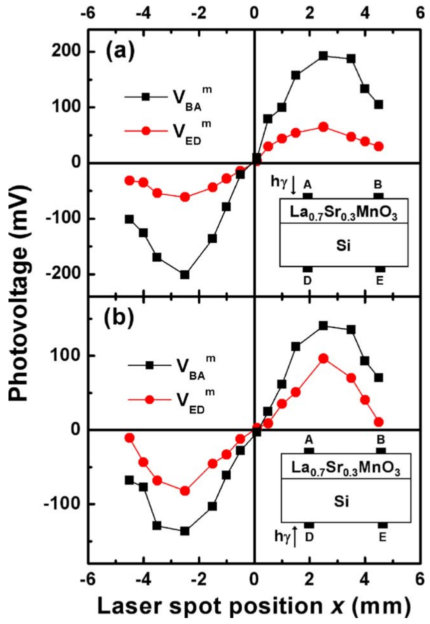

FIG. 2. (Color online) Peak LPVs V_{BA}^{m} and V_{ED}^{m} as a function of the position of the laser spot in the *x* direction for irradiating the $La_{0.7}Sr_{0.3}MnO_3/Si$ junction through (a) the $La_{0.7}Sr_{0.3}MnO_3$ side and (b) the Si side. The insets display the schematic setup for LPV measurement. *A* (−3 mm), *B* (3 mm), *D* (−3 mm), and *E* (3 mm) denote the electrodes.

tive for any position of laser spot) measured in the irradiation on the opposite side of the sample shown as Figs. 1(a) and 1(b), we can also conclude that the thermoelectric effect does not play an important role in the LPV we observed, as the LPVs were supposed to be reversed in the irradiation on the opposite side due to the reversed temperature gradient in the direction perpendicular to the interface of the sample.[15]

For further studying the Dember effect in silicon based oxide heterostructure, similar measurement taken in the heterostructure $La_{0.7}Sr_{0.3}MnO_3/Si$ we fabricated by laser molecular beam epitaxy technique was also carried out. $La_{0.7}Sr_{0.3}MnO_3/Si$ is also a *p*-*n* heterojunction which structure and transport property have been studied.[2] The corresponding results are shown in Figs. 2(a) and 2(b). Comparing Fig. 2 with Fig. 1, we can see that much larger Dember effect induced LPV occurs in $La_{0.7}Sr_{0.3}MnO_3/Si$ than that in $La_{0.9}Sr_{0.1}MnO_3/SNTO$. If the electrons are excited far in the depth of the band, the photoelectrons gain much kinetic energy from the large amount of excess energy in the excitation. These conditions, as well as high electron mobility, enhance the Dember effect in the system.[12] As well known, the band gap of Si (≈1.1 eV) is much more narrow than that of SNTO (≈3.2 eV), which means that photoelectron has more kinetic energy gain in $La_{0.7}Sr_{0.3}MnO_3/Si$ than in $La_{0.9}Sr_{0.1}MnO_3/SNTO$ with excitation by a 308 nm (≈4.03 eV) laser. This explains why the Dember effect LPV we observed in $La_{0.7}Sr_{0.3}MnO_3/Si$ junction is much larger than that in $La_{0.9}Sr_{0.1}MnO_3/SNTO$ junction. The different absorption coefficients and the quantum efficiency for different semiconductors should be mainly responsible for the different amounts of laser induced carriers in different types of semiconductors. We can also see that the top value of V_{ED} in Fig. 1(b) is a little bit smaller than that in Fig. 1(a). We believe that this is due to the surface scattering with the irradiation on SNTO side, as the substrate of SNTO we used was only single surface polished, which means the radiated surface is quite rough, so that the absorption of photons is smaller in this case. Contrarily, the Si substrate we used was double side polished, so that the top value of V_{ED} in Fig. 2(b) is a little bit larger than that in Fig. 2(a).

To confirm the above reason for the difference between the LPV in $La_{0.9}Sr_{0.1}MnO_3/SNTO$ and that in $La_{0.7}Sr_{0.3}MnO_3/Si$, the LPV measurements for *n*-SNTO and *n*-Si substrates have been also carried out. It is revealed that the same dependence of the sign and magnitude on the laser spot position as that of V_{ED}^{m} under the irradiation in the SNTO or Si side for a *p*-*n* junction. From the measurement, we find LPV in *n*-Si is much larger than that in *n*-SNTO, which further confirmed the above explanation that Dember effect induced LPV in the heterostructure of $La_{0.7}Sr_{0.3}MnO_3/Si$ is much larger than that in the heterostructure of $La_{0.9}Sr_{0.1}MnO_3/SNTO$. This experiment further supports the present mechanism in oxide *p*-*n* heterostructures.

In conclusion, the present results clearly demonstrate that both majority and minority carriers induced by laser pulse in oxide *p*-*n* junction play important roles in the formation of LPV, which is different from the understanding for LPV in conventional semiconductor *p*-*n* junction in which only majority carriers and the built-in field dominate the formation of LPV. Much larger LPV produced in heterostructures than that in simple samples strongly suggests some potential applications of the Dember effect in heterostructures, and the mechanism of this difference between the LPV in heterostructures and that in simple samples remains an open question. Potential applications of this Dember effect on photoelectric detector or even terahertz radiation in the presented heterostructures are expected.

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