Ultrafast dynamics of photoexcited carriers in multiband semiconductors SnSe and Sn$_{1-x}$Na$_x$Se

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We report time-resolved and angle-resolved photoemission spectroscopy on SnSe and Sn$_{1-x}$Na$_x$Se ($x = 0.015$) which currently attract great interest due to their extremely high thermoelectric performance. The valence band of SnSe exhibits upward energy shift of $\sim$0.2 eV due to the photoexcitation while that of Sn$_{1-x}$Na$_x$Se does not show appreciable energy shift. As for SnSe, within 50 fs after the pump pulse arrival, the conduction band bottom is observed just above the valence band maximum near the Z point while the conduction band is located around 0.5 eV above the Fermi level near the $\Gamma$ point. This suggests that the band gap is collapsed by the photoexcitation due to downward and non-rigid band shift of the conduction band. At 80 fs after the pump pulse arrival, the band gap is recovered, and the conduction electrons are almost depleted with some residual populations around minimum points of the conduction bands.

Thermoelectric power generation is one of the key technologies for sustainable and secure energy supply. Among the various candidate materials for thermoelectric power generation devices, the multiband IV-VI semiconductors such as PbQ ($Q=$Se, Te) [1–5] and SnQ ($Q=$Se, Te) [6, 7] have been attracting great interest due to their high thermoelectric performance with relatively good electrical conductivity, enhanced Seebeck coefficient, and strongly suppressed lattice thermal conductivity. The large Seebeck effect is derived from the multiple valence band maxima and the conduction band minima in the multiband band structure. The suppression of lattice thermal conductivity is associated with the lattice disorder and anharmonic dynamics which are derived from the lone pair due to the Pb(Sn) $s$ and $p$ orbitals [8]. In SnSe, it has been proposed that the small energy separation between the multiple valence band maxima plays essential roles for the enhancement of Seebeck coefficient [6]. The interplay between the lone pair effect and the multiband electronic structure provides unique electron-lattice coupling to the PbQ and SnQ systems. It is expected that the specific electron lattice coupling manifests itself in ultrafast optical response. In this context, it would be interesting to investigate optically induced electronic and lattice dynamics of the thermoelectric PbQ and SnQ systems by means of time-resolved spectroscopy. In particular, time- and angle-resolved photoemission spectroscopy (TARPES) enables us to probe dynamics of photoexcited carriers and temporal evolution of band structure.

SnSe has a layered structure constructed with strong bonds along the $b$-$c$ plane and weak bonds along the $a$-axis as shown in Fig. 1(a) [9]. Since the discovery of ultrahigh thermoelectric performance in Na-doped SnSe [10], the electronic structure of SnSe and Na-doped SnSe with the multiple valence band maxima has been extensively studied by means of band structure calculations and angle-resolved photoemission spectroscopy [11–18]. The observed valence band structure is basically consistent with the theoretical predictions as well as the transport properties [10, 19, 22]. Compared to the valence band, the nature of the conduction band of SnSe and Na-doped SnSe has not been studied so far. In addition, dynamics of photoexcited carriers may provide useful information for understanding of the unusual electronic and lattice properties of SnSe. In the present work, we report a TARPES study on SnSe and Sn$_{0.985}$Na$_{0.015}$Se single crystals. In addition to the information on the conduction band, the present results provide interesting insights on the ultrafast dynamics of the photoexcited electrons in SnSe which would be related to the unusual electron lattice coupling in the system.

Single crystals of SnSe and Sn$_{0.985}$Na$_{0.015}$Se were grown as reported in the literature [10]. TARPES experiments have been performed at LASOR, Institute for Solid State Physics, University of Tokyo. The base pressure of the spectrometer was in the $9 \times 10^{-11}$ Pa. The samples were cleaved and measured at 80 K. The energy of the Ti:sapphire laser was 1.55 eV and the energy of the probe light was 21.7 eV. The repetition rate was set to 10 kHz, and the fluence of the incident pump was set...
FIG. 1. (color online) (a) The Pnma crystal structure of SnSe created by VESTA \[32\]. (b) The Brillouin zone of SnSe. $k_y$ ($k_z$) represents wave number along the ΓY (ΓZ) direction. The circles correspond to the valence band maximum points of the $\alpha$, $\beta$, and $\gamma$ bands. Photoemission intensity distributions as functions of energy and $k_y$ before photoexcitation for (c) $\alpha$ band cut of SnSe, (d) $\gamma$ band cut of SnSe, (e) $\alpha$ band cut of Sn$_{0.985}$Na$_{0.015}$Se, (f) $\gamma$ band cut of Sn$_{0.985}$Na$_{0.015}$Se, whose momentum locations are shown as solid lines in (b).

FIG. 2. (color online) Time evolution after photoexcitation of the photoemission intensity distributions as functions of energy and $k_y$ for (a) $\alpha$ band cut and (b) $\gamma$ band cut in SnSe. The photoemission intensities are plotted in the logarithmic scale in order to emphasize the photo-induced change.

The bandgap to $\sim$0.95 mJ cm$^{-2}$. The pump and probe photons were p-polarized relative to the sample surface. The photoelectrons were detected by using a hemispherical electron analyzer ( Scienta Omicron R4000). The total energy resolution was 227 meV and time resolution was set to 80 fs. Local density approximation (LDA) calculations were performed by QUANTUM ESPRESSO 5.30 \[22\]. Pseudopotentials of Sn.pz-dn-rrkjus.psl.0.2.UPF and Se.pz-n-rrkjus.psl.0.2.UPF were used for the calculations.

Figures 1(c) and (d) show the photoemission intensity distributions as functions of energy and $k_y$ for SnSe before the pump pulse arrives. Here, $k_y$ represents wave number along the ΓY direction. The valence band maxima near the Z point are included in the cut of Fig. 1(c) ($\alpha$ band cut). $\gamma$ band cut shown in Fig. 1(d) includes the zone center and the valence band maxima near the Y point. Figures 1(e) and (f) show the photoemission intensity distributions as functions of energy and $k_y$ for Sn$_{0.985}$Na$_{0.015}$Se before the pump pulse arrives. The valence band maxima near the Z point are more clearly observed in SnSe than in Sn$_{0.985}$Na$_{0.015}$Se. On the other hand, the valence band maxima near the Y point are rather clear in Sn$_{0.985}$Na$_{0.015}$Se. This is consistent with the previous ARPES result in which the valence band maxima near the Y point was more clearly observed in Sn$_{0.985}$Na$_{0.015}$Se than SnSe \[13\].

Figure 2(a) shows the relaxation process after the pump pulse arrival for the photoemission intensity distribution along the $\alpha$ band cut of SnSe. In order to emphasize the photo-induced change, the logarithm of the photoemission intensity is plotted. Within 50 fs after the photoexcitation, a downwardly convex parabolic conduction band is observed just above the valence band maxima. This indicates that the band gap is closed in the photoinduced phase. At 80 fs after the photoexcitation,
the photoexcited electrons are almost depleted suggesting that the band gap is recovered. As for the \( \gamma \) band cut including the \( \Gamma \) point (Fig. 2(b)), a flat conduction band is observed around 0.5 eV above the Fermi level within 50 fs after the photoexcitation. At 80 fs, the photoexcited carriers are almost depleted probably due to the reformation of the band gap. Interestingly, at 133 fs and 587 fs from the photoexcitation, residual populations of the conduction bands are observed at three points along the cut. The three points may correspond to the three local minima of the conduction bands predicted for the Pnma phase.

Figures 3(a) and (b) show the difference spectra obtained by subtracting the intensity distribution before the pump pulse arrival from those after the arrival. In the \( \alpha \) band cut in Fig. 3(a), a downwardly convex parabolic band is observed within 50 fs after the pump pulse arrival, again indicating the band gap collapse due to the photoexcitation. The intensity distribution at 27 fs roughly agrees with the LDA band structure calculation which is shifted downwards in order to adjust the conduction band bottom in the \( \alpha \) band cut to the experimental result. On the other band, in the \( \gamma \) band cut in Fig. 3(b), the intensity distribution at 27 fs does not agree with the LDA calculation which is shifted downwards in the same way. At or later than 80 fs, the band gap is recovered and the photoexcited carriers are almost depleted except the residual populations around 1 eV above the Fermi level. In Figs. 3(a) and (b), the intensity distributions at 587 fs are compared with the LDA band structure calculations which are shifted upwards in order to adjust the conduction band bottom in the \( \gamma \) band cut to the experimental result. In addition to the dramatic change of the conduction band, the entire valence band is shifted upwards due to the photoexcitation. The energy shift survives up to 587 fs indicating that the residual conduction band electrons (and the valence band holes) are enough to induce the energy shift of the valence band.

The photoinduced band gap collapse in SnSe resembles that observed in \( \text{Ta}_2\text{NiSe}_3 \) [25]. \( \text{Ta}_2\text{NiSe}_3 \) is considered to be a candidate of excitonic insulator [24, 30]. In the photoinduced gap collapse of \( \text{Ta}_2\text{NiSe}_3 \), the photoexcited carriers screen the Coulomb interaction between the valence band hole and the conduction band electron which provides the insulating ground state. A similar mechanism is proposed for another excitonic insulator candidate \( \text{TiSe}_2 \) [31]. As for SnSe, the photoinduced band gap collapse may indicate electron-hole correlation effect on the formation of its band gap. However, there is no indication of excitonic instability in SnSe. Here, we speculate that the strong Sn 5s, 5p-Se 4p hybridization with the lone pairs formation [8] is destroyed by the photoexcited carriers. If the Sn 5s, 5p-Se 4p hybridization is weakened and the chemical bonds in the Sn-Se polyhedral are suppressed, then the band gap is expected to be reduced or collapsed. For example, in the Cmcm phase with stacked rocksalt layers, the magnitude of the band gap is predicted to be 0.464 eV while it is 0.829 eV in the Pnma phase with strong distortion due to lone pairs in the GW calculations [22].

It is expected that Na substitution for Sn disturbs the strong Sn 5s, 5p-Se 4p hybridization with the lone pair formations. Therefore, it would be interesting to investigate the effect of Na doping on the ultrafast dynamics of photoexcited carriers. Figure 4(a) shows the relaxation process after the pump pulse arrival for the photoemission intensity distribution along the \( \alpha \) band cut of \( \text{Sn}_{0.985}\text{Na}_{0.015}\text{Se} \). Firstly, the valence band of Na-doped SnSe does not show appreciable energy shift while SnSe exhibits upward energy shift of \( \sim 0.2 \) eV by the photoexcitation. The lack of valence band energy shift may indicate that the numbers of photoexcited electrons and holes are much smaller in Na-doped SnSe than in SnSe. Secondly, unlike SnSe, no parabolic conduction band is observed in Na-doped SnSe. Instead, the conduction band around 0.5 eV above the Fermi level is populated by photoelectrons.
FIG. 4. (color online) Time evolution after photoexcitation of the photoemission intensity distributions as functions of energy and $k_y$ for (a) $\alpha$ band cut and (b) $\gamma$ band cut in Sn$_{0.985}$Na$_{0.015}$Se. The photoemission intensities are plotted in the logarithmic scale in order to emphasize the photo-induced change.

In conclusion, we have performed TARPES on SnSe and Sn$_{1-x}$Na$_x$Se with extremely high thermoelectric performance in order to investigate their conduction bands as well as ultrafast dynamics of photoexcited electrons. The valence band of SnSe exhibits upward energy shift due to the photoexcitation while that of Sn$_{0.985}$Na$_{0.015}$Se does not show appreciable energy shift. In SnSe, the conduction bands are highly populated by photoexcited electrons within 50 fs from the pump pulse arrival. The conduction band bottom is observed just above the valence band maximum near the Z point indicating collapse of the band gap. On the other hand, the conduction band is located around 0.5 eV above the Fermi level near the $\Gamma$ point. The photoinduced effect on the conduction band would be related to suppression of lone pair. At 80 fs after the pump pulse arrival, the band gap is recovered, and the photoexcited electrons are almost depleted both in SnSe and Sn$_{0.985}$Na$_{0.015}$Se. However, some residual electrons are observed in local minima of the conduction bands. It is suggested that the band gap is reestablished by the recovery of lone pair, and the residual electrons are concentrated at the local minima.

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