Strain-induced Giant Second-harmonic Generation in Monolayered 2H-MoX\textsubscript{2} (X=S,Se,Te)

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(Dated: April 28, 2015)

Dynamic second-order nonlinear susceptibilities, $\chi^{(2)}(2\omega,\omega,\omega) \equiv \chi^{(2)}(\alpha)$, are calculated here within a fully first-principles scheme for monolayered molybdenum dichalcogenides, 2H-MoX\textsubscript{2} (X=S,Se,Te). The absolute values of $\chi^{(2)}(\alpha)$ across the three chalcogens critically depend on the band gap energies upon uniform pressure, yielding the highest $\chi^{(2)}(0) \sim 140$ pm/V for MoTe\textsubscript{2} in the static limit. Under this uniform in-plane stress, 2H-MoX\textsubscript{2} can undergo direct-to-indirect transition of band gaps, which in turn substantially affects $\chi^{(2)}(\alpha)$. The tunability of $\chi^{(2)}(\alpha)$ by either positive or negative strain is demonstrated especially for two important experimental wavelengths, 1064 nm and 800 nm, where resonantly enhanced non-linear effects can be exploited: $\chi^{(2)}$ of MoSe\textsubscript{2} and MoTe\textsubscript{2} approach $\sim 800$ pm/V with -2\% strain at 1064 nm.

PACS numbers: 75.30.Gw, 75.50.Cc, 75.70.Tj

Since the discovery of graphene, two-dimensional materials have attracted great attention for their intriguing physics such as tremendous transport properties, low mobility and high conductivity\textsuperscript{[1-4]}. However, their semi-metallic character due to the absence of a band gap, hinders the efforts to replace graphene for silicon based technology. There have been a lot of research efforts to artificially create non-vanishing band gap in graphene by introducing defects, ripples, and so forth.

MoS\textsubscript{2}, another two-dimensional material, has also revealed fascinating properties found in graphene – high mobility and mechanical strength\textsuperscript{[5]}, and even superconductivity\textsuperscript{[6]}. Despite its similar structure to graphene, the hetero-atomic constitution of MoS\textsubscript{2} naturally breaks such valley or sublattice degeneracy, unlike graphene, where the sublattice symmetry in the hexagonal lattice enforces degeneracy at valleys in the Brillouin zone. As a result, the MoS\textsubscript{2} band gap is finite, as large as 1.3 eV\textsuperscript{[5, 7]}. Other materials in the same family, the so-called transition-metal dichalcogenides (TMDs), or 2H-MoX\textsubscript{2} (X=S,Se,Te), possess similar properties due to their equivalent structures.

Bulk MoS\textsubscript{2} crystallizes in the hexagonal structure with centrosymmetric space group $D_{6h}$. While another polytype, the 1T structure also exists with octahedral coordination, we focus solely on the 2H structure with trigonal-prismatic coordination in this work. The 2H structure consists of two unit layers as illustrated in Fig. 1 where one unit layer has one Mo and two S atoms, each taking A and B sites, respectively. The Mo-X bonds are strongly covalent, and the sandwich layers are weakly coupled by van der Waals interactions.

As graphene has been easily isolated from graphite, few-layer MoS\textsubscript{2} has also been successfully exfoliated from bulk MoS\textsubscript{2}. Interestingly, while bulk MoS\textsubscript{2} has an indirect band gap, the isolated monolayer-MoS\textsubscript{2} reveals a direct band gap\textsuperscript{[5, 7]}. This indirect-to-direct transition of the band gap is not restricted to MoS\textsubscript{2}; other 2H-MoX\textsubscript{2} (X=S,Se,Te) exhibit the indirect-to-direct transition of the band gap in their monolayered structure\textsuperscript{[8]}. Among many promising properties of MoS\textsubscript{2}, the feasibility of achieving large second-harmonic-generation (SHG) coefficients has recalled intensive attention for an immediate practical application. In the exfoliated MoS\textsubscript{2} film, a strong second-order non-linearity is observed in the odd-layer MoS\textsubscript{2} as a consequence of broken centro-symmetry, which vanishes for the even-layer ones due to the centro-symmetry\textsuperscript{[9]}. To date, several research groups have conducted measurements on the second-order non-linearity on monolayer MoS\textsubscript{2}. However, their values differ by three orders of magnitude from one measurement to another. The origin of this discrepancy is still under debate\textsuperscript{[10]}, whether it stems from the probing method or from different fabrication methods such as exfoliation or chemical vapor deposition (CVD) method. Nevertheless, unarguably large SHG coefficient, reaching at least

\begin{figure}[h]
\centering
\includegraphics[width=0.6\textwidth]{figure1.png}
\caption{(color online) (a) Structure of the bulk TMD 2H-MoX\textsubscript{2} (X=S,Se,Te), where the unit cell is shown in the dotted box. (b) Top- and (c) side-view of the structure of the monolayer of 2H-MoX\textsubscript{2}. Red and yellow spheres denote Mo and chalcogen (S,Se,and Te) atoms, respectively.}
\end{figure}
100 pm/V, makes MoS$_2$ very promising for non-linear optics applications.

In this letter, using fully first-principles calculations of 2H-MoX$_2$ (X=S,Se,Te), the electronic structure and the SHG coefficients are investigated. In-plane strain in a uniform manner alters band gaps, which in turn changes the SHG coefficients. Despite qualitative similarities of the electronic structure among the 2H-molybdenum dichalcogenides, the resultant frequency-dependent SHG coefficients, $\chi^{(2)}(\omega)$, show some differences in their spectra. The tunability of $\chi^{(2)}$ by chalcogen atoms, as well as the in-plane strain, will be addressed.

First-principles calculations were carried out using the highly precise full-potential linearized augmented plane wave (FLAPW) method. The local density approximation (LDA) is employed for the exchange-correlation potential. Spin-orbit coupling is explicitly included in a semi-relativistic way. Muffin-tin radii of 2.25 (Mo) and 2.00 a.u. (chalcogens) are chosen. Cutoffs for wave function and potential representations are 14.06 and 144 Ry., respectively. The angular momentum expansion of charge density and potential inside the MT sphere are done for $\ell \leq 8$. Summation in the Brillouin zone is performed using Monkhorst-Pack scheme with a $45 \times 45 \times 15$ $k$ point mesh, which includes high-symmetry $K$ and $M$ points. To reduce artificial layer-layer interactions, adjacent layers are separated by 20 Å. We employed the experimental lattice constants for the present work, $a=3.160$ Å (MoS$_2$), 3.299 Å (MoSe$_2$), and 3.522 Å (MoTe$_2$), respectively. For simplicity, band gap correction beyond LDA is not employed and the exciton effects are ignored.

For calculations of the second-harmonic generation (SHG) coefficients, we employ the method by Aversa and Sipe, which has been successfully proved in other works. The imaginary part of the second harmonic susceptibility tensor, $\chi^{(2)}_{abc}$, is calculated as

$$\chi^{(2)}_{abc}(\omega) = \frac{e^3}{2\pi m^* h^2 \epsilon_0} \sum_{c,x,y} \sum_k \left[ \frac{P_{vc}}{\omega^2 - \omega_v^2} \delta(2\omega - \omega_v,\omega_v) \right]$$

where $(a,b,c)$ represent the cartesian $(x,y,z)$, and $c,v$ stands for the conduction and the valence band, respectively, $P_{ij}$ is matrix tensor for state indices $i$ and $j$, and $l \neq c,v$ denotes the intermediate virtual state, which can be either the virtual electron or hole state. $P_{lj} = \langle j|p_i|j \rangle$ is momentum matrix for state indices $i$ and $j$, and wave vectors for the Bloch state are suppressed. A $45 \times 45 \times 15$ $k$ mesh is also used for summation in Eq. (1) using the special $k$ point scheme. The corresponding real part of $\chi^{(2)}_{abc}(\omega)$ is obtained by the Kramers-Kronig transformation of the calculated imaginary part. Due to the hexagonal symmetry in monolayered 2H-MoX$_2$, there is only one non-vanishing component in the $\chi^{(2)}$ tensor in $D_3h$ symmetry: $\chi^{(2)} = \chi^{(2)}_{xxy} = -\chi^{(2)}_{yyx} = -\chi^{(2)}_{yxy}$.

The calculated band gaps of 2H-MoX$_2$ are shown in Fig. 2(a), where the direct (indirect) band gaps are shown in filled (empty) symbols. Upon pressure or lattice strain, band gaps decrease (increase) as the lattice expands (contracts). Noteworthy, there are indirect band gaps for expanded (MoS$_2$, MoSe$_2$) and contracted lattices (MoSe$_2$ and MoTe$_2$). This feature in connection to the band structure will be discussed later. We emphasize two facts: LDA usually underestimates the band gap, and calculated band gaps are larger than the experimental ones. This implies that the exciton binding energies are significant, at least 0.35 eV, 0.27 eV, and 0.03 eV for the MoS$_2$, MoSe$_2$, and MoTe$_2$, respectively.

The SHG coefficients for the static limit, $\chi^{(2)}(\omega = 0) \equiv \chi^{(2)}(0)$, as a function of different lattice constants are plotted in Fig. 2(b). $\chi^{(2)}(0)$ of MoS$_2$ increases monotonically as the lattice expands due to the smaller band gaps, reaching 97.04 pm/V for a +2% change. For MoSe$_2$ and MoTe$_2$, $\chi^{(2)}(0)$ also increases as the lattice expands. However, both cases have dips at -1% lattice. This is due to smaller band gap of -1% lattice with respect to -2%. Moreover, indirect band gaps of -2% lattice are much smaller than the direct ones of -1% lattice by 0.2 eV. Above all, the enhancement of $\chi^{(2)}(0)$ in most cases is well understood: lattice expansion decreases the band gap, which in turn increases $\chi^{(2)}(0)$. Interestingly, $\chi^{(2)}(0)$ of MoS$_2$ reaches almost 100 pm/V, whereas those of MoSe$_2$ and MoTe$_2$ exceed 100 pm/V with the maximum value as high as 170 pm/V.

For a more quantitative analysis, the band structures of 2H-MoX$_2$ are plotted in Fig. 3. [Band plots of other strains are provided in the Supplementary Information.] Important transitions from the valence band maximum (VBM) to the conduction band minimum (CBM) are labeled. $A$ denotes the transition from VBM ($K_{1L}$) to CBM ($K_{1U}$) at the $K$ point. $B$ denotes from the spin-orbit split states ($K_{2L}$) to $K_{1C}$. $C$ and $D$ are transitions at $M$ and $\Gamma$, respectively. Near the midpoint...
between K-Γ in the valence band is labelled as $T_v$. Red arrows connect valence band maximum (VBM) to conduction band minimum (CBM):

As mentioned previously, indirect band gaps are shown for expanded (contracted) lattices of MoS$_2$ (MoSe$_2$ and MoTe$_2$). In all cases, direct band gaps occur at K. On the other hand, indirect gaps of MoS$_2$ occur from the $\Gamma_{v1}$ to $K_{c1}$; those in MoSe$_2$ and MoTe$_2$ occur from $T_v$ to $K_{c1}$. SOC splittings of MoS$_2$, MoSe$_2$, and MoTe$_2$ are of 151, 190, and 229 meV, respectively, which are energy differences of $K_{v1}$ and $K_{c2}$. As with a previous study [8, 22], VBM and CBM consist mainly of Mo $d$ states with a weak contribution of chalcogen $p$ states. In $D_{3h}$ symmetry, $d$ states have three irreducible representations: $xz/yz$, $xy/x^2-y^2$ and $z^2$. More specifically, at the K point, the VBM and CBM are predominantly derived from $xy/x^2-y^2$ and $z^2$ states, respectively. Near $\Gamma$ point, $z^2$ ($xz/yz$) dominates the VBM (CBM). For midpoint of K-Γ, $T_v$, while the CBM is mainly of $x^2-y^2/xy$ state, the VBM is of a mixture of $x^2-y^2/xy$ and $xz/yz$. In MoSe$_2$ and MoTe$_2$, on the other hand, while dominant states in $K_{v1,2}$, $K_c$, and $\Gamma_{c,v}$ are similar to MoS$_2$, the valence band of the midpoint, $T_v$, consists of a mixture of $xz/yz$ and $z^2$. We note that indirect gaps in MoS$_2$ occur such that $\Gamma_v$ shifts upward with lattice contraction, while in MoSe$_2$ and MoTe$_2$, $T_v$ moves upward with lattice expansion. Since the $d$ contribution of $\Gamma_c$ in MoS$_2$ and of $T_v$ of MoSe$_2$ and MoTe$_2$ are both $xz/yz$, contraction of lattice in MoS$_2$ acts similarly as expansion in MoSe$_2$ and MoTe$_2$. The frequency-dependent dispersion of the SHG coefficients, $\chi^{(2)}(\omega)$, are plotted in Fig. 3 for different strains. The frequency window is chosen from 0 to 2.5 eV, which includes the important frequency range (IR) of 1064 nm (1.16 eV) and 800 nm (1.54 eV). [See Supplementary Information, to refer frequency-dependent $\chi^{(2)}(\omega)$ for a wider range of frequencies.]

For the MoS$_2$, in the absence of strain, the large peak around 2.0 eV reaches 600 pm/V just above the band edge around 1.0 eV. Below the band edge ($E$), two smaller peaks appear at half of the band gap ($H$) and 0.2 eV below the band gap. From the band analysis, also in qualitative agreement with another study on the SHG coefficients of MoS$_2$[10, 13], these two peaks are from $A/2$, $B/2$, $C/2$, $D/2$, respectively, where the division by two indicates half of the energy values of the corresponding transitions. The enhancement of $\chi^{(2)}(\omega)$ is apparent for +1 and +2% lattice change at a frequency much larger than 2.0 eV. On the other hand, large peaks also occur at lower frequencies for contracted lattices. In particular, the peak around the IR frequency range is prominent: $\chi^{(2)} \sim 600$ pm/V.

Four distinct peaks are apparent for $\omega < 4$ eV in the case of MoSe$_2$ with zero strain. Two peaks at $H$ and at 3 eV are small, and the peak just below $E$ is pronounced, while that at 2 eV is rather broadened. For +1% strain, the first peak at $H$ is sharpened, while at $E$ it is still sharp but reduced. On the other hand, for +2% strain, there is a dip between peaks at $H$ and $E$, where that at the band edge becomes broadened with third peak gets more pronounced. The change of spectrum between these two stretched strains originates from the change of the bands: the top valence bands remains almost unaltered, while the conduction band changes, though a little bit, between $\Gamma$-M and K-Γ. For the contracted lattices, the direct band gap becomes indirect, where the CBM and the $K_{c1}$ are very close in energy, hence the two peaks below $E$ tend to merge.

For the zero strain of MoTe$_2$, two peaks are clearly noticeable, where the first peak is just below $E$, while the second peak is well above $E$ near 2 eV. For positive strains, two peaks slightly shift to lower energies. More specifically, for +2% strain, the first peak is a little smoothened between $H$ and $E$, whereas the second peak just below 2 eV is more en-
hanced. On the other hand, for negative strains, the first peak is split into two - one above \( E \), the other near \( H \) with enhancement with respect to the zero strain case. We note that \( \chi^{(2)}(\omega) \) within IR frequency range approaches 800 pm/V for both MoSe\(_2\) and MoTe\(_2\) when lattice is contracted by -2%.

In conclusion, we predict using first-principles calculations giant non-linear second-harmonic susceptibilities of the molybdenum-di-chalcogenides, 2\( H \)-MoX\(_2\) (X=S,Se,Te). We have found that band gaps can be altered by lattice strains: Expansion (contraction) of the lattice leads to a decrease (increase) of the band gaps. As a result, static values of the second-harmonic susceptibilities, \( \chi^{(2)}(\omega) \), can be altered by lattice strains. Frequency-dependent SHG coefficients, \( \chi^{(2)}(\omega) \), for different strains are also investigated, where the peak structure strongly depends on little changes in the electronic structure. Thus, we have shown that large values of \( \chi^{(2)} \) are accessible by applying lattice strains for IR frequency range.

SHR is grateful to Joonik Jang, Yongsoo Kim, Y.D. Jho for fruitful discussions. Work at Northwestern was supported by the Department of Energy (DE-FG02-88ER45382). Supercomputing time by NERSC is also acknowledged. Work at University of Ulsan is supported by Priority Research Centers Program (2009-0093818) and the Basic Science Research Program (2009-0088216) through the National Research Foundation funded by the Ministry of Education of Korea.

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