Phonon Softening and Direct to Indirect Bandgap Crossover in Strained Single Layer MoSe$_2$

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(Dated: April 10, 2013)

Motivated by recent experimental observations of Tongay et al. [Tongay et al., Nano Letters, 12 (2012)] we show how the electronic properties and Raman characteristics of single layer MoSe$_2$ are affected by elastic biaxial strain. We found that with increasing strain: (1) the $E'$ and $E''$ Raman peaks ($E_{1g}$ and $E_{2g}$ in bulk) exhibit significant red shifts (up to $\sim$30 cm$^{-1}$), (2) the position of the $A'_1$ peak remains at 180 cm$^{-1}$ ($A_{1g}$ in bulk) and does not change considerably with further strain, (3) the dispersion of low energy flexural phonons crosses over from quadratic to linear and (4) the electronic band structure undergoes a direct to indirect bandgap crossover under $\sim$3% biaxial tensile strain. Thus the application of strain appears to be a promising approach for a rapid and reversible tuning of the electronic, vibrational and optical properties of single layer MoSe$_2$ and similar MX$_2$ dichalcogenides.

PACS numbers: 81.16.Pr, 68.65.Pq, 66.30.Pa, 81.05.ue

I. INTRODUCTION

The discovery of graphene\cite{Novoselov2004} is expected to play an important role in future nanoscience and nanotechnology applications. Recent advances in nanoscale growth and mechanical exfoliation techniques have led not only to the fabrication of high-quality graphenes but also to the emergence of several new classes of two-dimensional (2D) structures such as ultra-thin transition metal dichalcogenides (TMDs). Just like graphene TMDs have hexagonal crystal structure composed of layers of metal atoms (M) sandwiched between layers of chalcogen atoms (X) with stoichiometry MX$_2$. TMDs have electronic semi-conducting or metallic properties and most of bulk TMDs possess indirect band gaps of the order 1-2 eV.\cite{Raghu2010} The synthesis of several TMDs has been realized experimentally\cite{Kirilyuk2010} and the stability and electronic properties of various single layer dichalcogenides was recently reported.\cite{Huang2010} Recent studies of several semiconducting TMDs such as MoSe$_2$, WS$_2$, MoTe$_2$ and MoS$_2$ have shown that the band gap increases and transforms to a direct band gap with decreasing number of layers.\cite{Huang2010, Kong2009, Liu2010} These sizeable band gaps make them well suited for electronic and optical applications such as transistors, photodetectors and electroluminescent devices. Another unique feature of two-dimensional ultra-thin materials is the possibility to apply large reversible elastic strain. It has been shown that graphene can be strained up to 20 % of its ideal structure with only small changes in its electronic band structure, which is in contrast to TMDs.\cite{Huang2010, Kong2009, Liu2010}

The most recent efforts have been directed towards the synthesis and manipulation of molybdenum diselenide (MoSe$_2$) single layers. In addition to preliminary reports on synthesis of few-layer MX$_2$ structures\cite{Tongay2011, Tongay2012, Tongay2012b} Tongay et al. demonstrated that a single layer of MoSe$_2$ possesses a direct optical gap of 1.55 eV and exhibits good thermal stability.\cite{Tongay2011} However, to our knowledge, no research exists addressing the question of how electronic properties and lattice dynamics of single layer MoSe$_2$ are affected by strain. In the present work, we investigate the effect of biaxial strain on the electronic and vibrational properties of single layer MoSe$_2$ structures. Our calculations revealed that applying biaxial strain is able to tune the Raman characteristics and electronic band structure of single layer MoSe$_2$. We expect that this study will offer new opportunities for strain-engineered nanoscale optoelectronic device applications.

II. COMPUTATIONAL METHODOLOGY

Calculations of physical properties of equilibrium and strained structures were carried out in the framework of density functional theory (DFT), using the plane-wave self-consistent field (PWSCF) code as implemented in the QUANTUM-ESPRESSO package.\cite{QE} The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was used for the exchange-correlation potential.\cite{QE} A plane-wave kinetic energy cutoff of 40 Ry and density cutoff of 400 Ry were used. Brillouin zone integration was performed using a shifted $27\times27\times1$ Monkhorst-Pack mesh.\cite{QE} To eliminate the interaction emerging from periodic boundary conditions calculations are performed with a large unitcell including 12 Å vacuum space between adjacent MoSe$_2$ single layers. Ground states and total energies of all systems were obtained after full geometry relaxation with forces on the atoms smaller than 0.02 eV/Å. Phonon frequencies and phonon eigenvectors were calculated in a $4\times4\times1$ q-grid using the density functional perturbation theory (DFPT).\cite{DFPT}
In comparison with single layer MoS$_2$, i.e., MoSe$_2$, branches in the whole Brillouin Zone have positive values required restoring force against atomic distortions. Additionally, the larger atomic radius of the Se atoms. In Fig. 1(a) inset: comparison of the band edges calculated by GGA, GGA+SO and LDA.

### III. RESULTS AND DISCUSSION

#### A. Single Layer MoSe$_2$

Atomically thin MoSe$_2$ is the most recently synthesized member of the ultra-thin transition metal dichalcogenides. A single layer structure of MoSe$_2$ can be viewed as a 3-layer stacking of Mo and Se atoms wherein molybdenum atoms are sandwiched between layers of trigonally arranged selenium atoms. In this configuration, known as 1H structure, each Mo atom is coordinated to six Se atoms. In the equilibrium geometry of the single layer MoSe$_2$, the Mo-Se distance, the Se-Se distance and the lattice constant of the hexagonal unit cell are calculated to be 2.528, 3.293 and $|a|$=3.321 Å, respectively. Thus, in comparison with single layer MoS$_2$ having lattice constant 3.12 Å, MoSe$_2$ has a larger atomic structure due to the larger atomic radius of the Se atoms. In Fig. 1(a) we present the calculated phonon dispersion and vibrational characteristics of R-active modes of single layer MoSe$_2$. It is seen that the frequencies of all phonon branches in the whole Brillouin Zone have positive values i.e., MoSe$_2$ crystal can remain stable by generating the required restoring force against atomic distortions. Although the synthesis of single layers of MoSe$_2$ have been achieved only on various substrates so far, energy optimization and phonon dispersion calculations show that freestanding MoSe$_2$ monolayers are quite stable.

The calculated band structure shown in Fig. 1(b) shows that the single layer MoSe$_2$ is a semiconductor with a direct bandgap at the K high symmetry point. The top of the valence band is mainly composed of Mo-$d_{(x^2-y^2)}$ orbitals and, albeit small, also by Mo-$d_{(xy,yz,zx)}$ and Se-$p_{(x,y)}$ orbitals. Though the electrons occupying 4$d$ and 5$s$ shells of a neutral Mo atom are treated as valence electrons, 5$s$ states have a negligible contribution even away from the Fermi level. However, it is seen that all Mo-$d$, Se-$p_{(x,y)}$ and Se-$p_{(z)}$ orbitals are hybridized to form the conduction band edge. Note that $x$ and $y$ component of the orbitals have the same energy due to the two-dimensional lattice symmetry. Due to the presence of another minimum in the conduction band edge between the Γ and K points we also used local density approximation (LDA) for the exchange correlation functional. Tongay et al. demonstrated that such a neighboring conduction band dip is quite sensitive to temperature-induced strain and layer-layer interaction. The lattice constant of a single-layer MoSe$_2$ is found to be smaller (3.22 Å) in LDA because of the overestimation of the strength of the covalent bonds. The inset of Fig. 1(b) shows a zoom of both LDA, GGA and GGA+SO band structures along the Γ-K-M path in the Brillouin zone. We see a splitting of the band edges at the vicinity of K point when including spin-orbit (SO) interactions. Interestingly, LDA predicts that single layer MoSe$_2$ is an indirect semiconductor where the top of the valence band is at the K point, and the bottom of the conduction band is found to be between the Γ and K points. It appears that the physically correct description of single layer MoSe$_2$ structure that was reported experimentally with a direct bandgap is achieved by using the GGA functionals. Therefore, in the rest of our study PBE calculations will be employed.

Although our PBE calculation captures the qualitative nature of the band edge states it underestimates the band gap. To correct the band gap we use the $G_0W_0$ approximation as implemented in the VASP package. It was shown before that this kind of calculation has to be converged with respect to the vacuum spacing. We calculate the quasi-particle shifts using (12×12×1) k-point grid with vacuum spacings of 15 Å, 20 Å, 25 Å, and 30 Å and then extrapolate them to infinity in a similar fashion as done in Ref. 24. Our $G_0W_0$ calculation results in a band gap value of 2.33 eV. Note that, excitonic effects are pronounced in 2D materials as we calculate the binding energy of the exciton in order to estimate the optical gap. Due to the parabolic shape of the conduction and valence bands we assume that the exciton has the Mott-Wannier character and the effective mass approximation can be used. Hole and electron effective masses calculated from the band structure are $m_h^* = 0.65$ and $m_e^* = 0.53$ (in units of electron mass). Moreover, we account for the 2D polarizability of the system using the model introduced by
B. Lattice Dynamics and Phonon Softening

While bulk MoSe$_2$ crystal has the D$_{6h}$ point group symmetry, it turns into D$_{3h}$ for single layer structure. Just like in MoS$_2$, lattice vibrations of single layer MoSe$_2$ is characterized by nine phonon branches including three acoustic and six optical branches. Analysis of lattice dynamics shows that the decomposition of the vibration representation at the $\Gamma$ point is $\Gamma = A'_1 + 4E' + 2E'' + 2A''_g$. While LA and TA acoustic branches have linear dispersion, the frequency of the out of plane flexural (ZA) mode has a quadratic dispersion in the vicinity of q=0. Near to the $\Gamma$ point the in-plane sound velocity of the LA and TA modes are found to be $1.5 \times 10^3$ and $0.9 \times 10^3$ m/s, respectively. It is also seen that differing from graphene’s phonon dispersion the acoustic and optical modes are well-separated from each other. Differing from MoS$_2$ and WS$_2$ structures in which the $A'_1$ mode is the highest Raman-active mode, in MoSe$_2$ the $A'_1$ mode is located in between the $E'$ and $E''$ modes. In Fig. 4(a) the atomic displacements of the R-active modes are presented. Interestingly, although recent Raman spectroscopy measurements of Tongay et al. revealed that only one characteristic Raman peak of single-layer MoSe$_2$ $E_{2g}$ is observable at 240 cm$^{-1}$, our symmetry analysis predicts the existence of two more Raman-active modes. Significantly decreased intensity of Raman peak around 290 cm$^{-1}$ can be explained by considering the coupling of in-plane counter-phase vibration of MoSe$_2$ with the SiO$_2$/Si substrate. Moreover, in experiment the disappearance of $E''$ ($E_{1g}$ in bulk) Raman shift around 170 cm$^{-1}$ is due to the inactivity of this vibrational mode to normally incident light.

Recent experiments on graphene and other few-layer materials have revealed that the application of biaxial and uniaxial tensile stress is possible by using flexible substrates. We will investigate now how the lattice dynamics of single layer MoSe$_2$ is affected by biaxial strain.

Fig. 2 shows phonon dispersion curves and the evolution of Raman peaks as a function of applied strain. Below 1% strain, the $E'$ branch of single layer MoSe$_2$ experiences $\sim 10$ cm$^{-1}$ softening which is larger than that of the $E_g$ mode (diatomic corresponding to $E'$) of graphene. It is seen that the low-energy flexural phonons (ZA) of unstrained single layer MoSe$_2$ turns almost in a linear dependence under 7% strain. Such a change in phonon dispersion implies a significant decrease in scattering of electrons by the flexural phonons and an increase in electron mobility for strained MoSe$_2$. For the $E'$ mode there is a small splitting at the $\Gamma$ point, as in slightly polar materials such as MoS$_2$ and WS$_2$. It is also seen that due to the weakening of the covalent bonds under strain the $E'$ and $E''$ modes (that correspond to the $E_{1g}$ and $E_{2g}$ in bulk MoSe$_2$, respectively) exhibit significant red shifts of about $\sim 30$ cm$^{-1}$. Especially, at the K point, the highest optical mode dips even below the band corresponding to the $E'$ mode. Another remarkable point is the $A'_1$ mode (corresponding to the $A_{1g}$ in bulk) that vibrates perpendicular to the applied strain which experiences a smaller softening and is almost pinned to 231 cm$^{-1}$ for strain values higher than 1%. Similar direction-dependent softening behavior was observed for various types of materials.

C. Strain-Induced Direct-to-Indirect Bandgap Crossover

In addition to strain-induced changes in the lattice dynamics, the electronic properties of single layer MoSe$_2$ may exhibit surprising deviations. Existence of a bandgap even in the monolayer structure shows strong bonding nature and the covalent character of MoSe$_2$ layers. Though the covalent bonds formed from valence electrons of Mo and Se atoms are not broken by elastic strain, the strength of the bond is weaken with the
increasing distance. Therefore band energies and dispersion can be expected to be strongly dependent on tensile strain. Evolution of the electronic band dispersion under finite biaxial strain (ε = 1 − 7%) is shown in Fig. 3. It is clearly seen that the band edges at the Γ and K symmetry points are influenced significantly by biaxial tensile strain. Up to 3% strain, single layer MoSe$_2$ remains a direct bandgap semiconductor with both the top of the valence band and the bottom of the conduction band located at the K point. However, when ∼3% strain is applied, as a result of the band shifting at the K point, two valence band edges with the same energy appear in the Brillouin Zone while the conduction band edge remains fixed in its original position. Here, with ∼3% strain one has both a direct (K→K) and an indirect (Γ→K) bandgap.

Such an interesting electronic structure may result in the presence of two types of holes having different effective masses and the coexistence of direct and indirect band transitions in the optical spectra. We also found that increasing further the strain results in the separation (and shifting) of the uppermost valence band towards the conduction band accompanied by the lowering of the conduction band dip at the K point. Moreover, the second conduction band edge located (between Γ and K) very close to the dip of the conduction band at the K point moves upwards in energy. In addition, band edges of MoS$_2$ also experiences similar effects with increasing tensile strain. The evolution of direct (K→K) and indirect (K→Γ and Γ→K) energy bandgaps under tensile stress are presented in Fig. 3(a). Both direct and indirect bandgaps decrease monotonically with increasing strain, however the rate of decrease is faster for the indirect bandgap. Note that, the variation of band gaps with increasing strain has the same qualitative behavior for PBE, PBE+SO and PBE+G$_0$W$_0$ calculations. We predict that the direct-to-indirect crossover takes place at 3−4% strain.

As a consequence of the strain-dependent transition of the valence band edge from the K to Γ point the effective mass of the holes (and electrons) propagating through the single layer MoSe$_2$ lattice changes dramatically. From Fig. 3 it is seen that while the mass of the electrons at the band edge does not change notably, the hole mass shows significant deviations under strain. Since the valence band edge is sharpened by biaxial strain the effective mass of the holes is decreased and after the bandgap crossover holes belong to the uppermost valence band at the Γ point inversely affected by increasing strain. Note that the holes under 7% strain are ∼2 times heavier than that for unstrained single layer MoSe$_2$.

In summary, motivated by the recent experimental study of Tongay et al. on single layer MoSe$_2$ we investigated the electronic properties and lattice dynamics of single layer MoSe$_2$ as a function of biaxial strain. We showed that GGA describes more accurately the electronic structure of single layer MoSe$_2$ and that LDA predicts the wrong nature of the bandgap. We found that monolayer MoSe$_2$ has four R-active characteristic modes: among these, the modes having counter-phase in-plane motion are significantly modified by strain and they soften by increasing strain. Red-shift in the position

FIG. 3: (Color online) Evolution of the electronic band dispersion of single layer MoSe$_2$ as a function of strain. Fermi level shown by red line is set to zero in the energy spectrum.

FIG. 4: (Color online) Evolution of (a) direct and indirect energy band gaps, (b) electron and hole effective mass, normalized to unstrained value ($m^*_e/m^*_{0,e}$ and $m^*_h/m^*_{0,h}$ ), under biaxial tensile strain. (c) Energy bandgaps calculated by using PBE+SO and PBE+G$_0$W$_0$ are shown by solid and dashed lines, respectively. Red, green and blue colors are used for transitions K→K, K→ΓK and Γ→K, respectively.
of these resonant Raman peaks are predicted to be \(~30 \text{ cm}^{-1}\). However the $A_2'$ branch (corresponds to the $A_1g$ in bulk) is negligibly influenced by strain. Moreover the linear dispersion of flexural mode in strained-MoSe$_2$ implies a reduced scattering of electrons from these ZA phonons. Our findings also revealed that the electronic band structure of single layer MoSe$_2$ also undergoes substantial changes under biaxial tensile strain. While the direct bandgap linearly decreases up to \(~3\%\) tensile strain, a direct to indirect bandgap crossover occurs when strain is further increased. Moreover the appearance of a positive curvature at the K point in the phonon spectra and possible metallicity for higher strain values suggests superconductivity in highly strained single layer MoSe$_2$. Our findings indicate that the bandgap of single layer MoSe$_2$ can be tuned reversibly by biaxial strain and is able to capture a broad range of the solar spectrum.

**IV. ACKNOWLEDGEMENTS**

This work was supported by the Flemish Science Foundation (FWO-Vl) and the Methusalem programme of the Flemish government. Computational resources were partially provided by TUBITAK ULAKBIM, High Performance and Grid Computing Center (TR-Grid e-Infrastructure). H. S. is supported by a FWO Pegasus Marie Curie Long Fellowship.

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