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Probing the interface strain in a 3D-2D van der Waals heterostructure

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The interaction at a van der Waals (vdW) epitaxial interface is perceived to be too weak to induce substantial elastic strain in films due to the weak nature of dipole-dipole interactions. Recent research on discovering giant strain in vdW heterostructures in 2D-2D configurations has reformed such an understanding. In this letter, the study on strain was extended to the regime of 3D-2D vdW heterostructures. Using temperature dependent Raman spectroscopy, the strain behaviors were revealed, through the change of phonon frequency, at a vdW epitaxial interface of CdS-mica. Although the interface was free of interactions for relatively thick CdS films, it was found that at least 0.4% strain can be borne at the interface when the film was only 6 nm thick and the strain was estimated to be 1.2% if a two-monolayer can be grown. The finding suggests that non-trivial strain could be enabled in 3D-2D vdW heterostructures if the thickness can be well-controlled, providing an avenue for strain engineering. This work also indicated a different changing tendency in the linewidth of phonon scattering as a function of temperature, which may be related to defects and serve as a reference for studying the linewidth of ultrathin films. *Published by AIP Publishing*. https://doi.org/10.1063/1.5000704

Strain engineering is an effective route to altering the physicochemical properties of materials, such as tuning bandgap,^{1,2} increasing the superconducting temperature,³ enhancing carrier mobility,⁴ increasing the pyroelectric coefficient,⁵ aligning the growth direction of nanowires,^{6,7} and enhancing catalysis efficiency.8 Traditionally, strain engineering is performed in chemical heteroepitaxy systems where elastic strain in large magnitude, up to $\sim 10\%$, can be obtained.⁹ In recent years, van der Waals epitaxy (vdWE) has attracted much attention because of the popularity in 2D materials. Different from chemical epitaxy, vdWE locks up the overlayers and substrates via dipole-dipole interactions.^{10,11} Compared to the strength of covalent or ionic bonding in chemical epitaxy, the overlayer-substrate interaction at a van der Waals (vdW) interface is intuitively considered to be weak. This is true as evidenced by the easiness in exfoliating layered materials. Many hence claimed early on that the overlayers grown on vdW substrates were free of interfacial strain, which has turned out to be debatable because weak is not equivalent to none. Studies have shown that strain could be generated even at the vdW interface of the two weakest 2D materials, namely, graphene and boron nitride.¹²⁻¹⁵ This fact indicates that the so-called "weak" dipole-dipole interaction is not that weak in the sense of creating strain. More importantly, it implies that all the benefits of strain engineering in traditional epitaxy could be potentially duplicated in the domain of the vdW interface, which will help bring the promise in 2D materials to fruition.

With strain demonstrated in 2D-2D heterostructures, we extended the scope by probing strain in 3D-2D heterostructures in this proof of concept study. Herein, the elastic strain at the interface of a 3D-2D vdW heterostructure was evaluated

with a case study on CdS-mica. The strain at the interface of CdS-mica was stimulated by changing temperature and monitored by Raman spectroscopy. Details regarding the CdS deposition and Raman setup can be found in the supplementary material. Three film thicknesses were tried, namely, 120, 30, and 6 nm. X-ray diffraction (XRD) reveals a wurtzite phase of the 120 nm CdS film in single crystal nature overlaying on mica, evident by the $\omega - 2\theta$ scan shown in Fig. 1(a) and azimuthal (φ) scan in Fig. 1(b). The epitaxial alignment between CdS and mica can be deduced from Fig. 1(b), which is consistent with the previous knowledge^{16,17} and as shown in Fig. 1(d). While no direct XRD measurement was conducted on 30 or 6 nm CdS film, it is reasonable to assume them to be the same crystals as the 120 nm film.

Figure 2 shows the room temperature (RT) Raman spectra of all CdS films on mica. For the thickest film, the first and second order longitudinal optical (LO) phonons of CdS can be recognized. Peaks contributed by mica, labeled by asterisk, can be found for 30 and 6 nm films. In the latter, the CdS LO mode is barely visible. To induce strain, temperature was then adjusted from RT to 77 K with an interval of 20 K. Note that the lowest temperature for the 6 nm CdS film was 97 K, since no usable Raman spectrum was obtained at 77 K. The LO mode frequencies and linewidths as a function of temperature will be quantitatively analyzed. The inset of Fig. 2 shows an atomic force microscopy (AFM) image of 6 nm CdS on mica with a root mean square (RMS) roughness of 2.5 nm, confirming that the films are continuous even at the smallest thickness.

Not only the strain in CdS-mica causes frequency shift in Raman spectra but also the thermal expansion and anharmonic phonon coupling of CdS itself can contribute when temperature changes. To clarify the contribution, a bulk single crystal



FIG. 1. (a) XRD $\omega - 2\theta$ scans of 120 nm CdS films on mica (green) and NaCl (blue). (b) Azimuthal scan of CdS (1011) ($2\theta = 28.4^{\circ}$, $\chi = 62^{\circ}$) with respect to mica (115) ($2\theta = 28.5^{\circ}$, $\chi = 44^{\circ}$) of the 120 nm CdS film on mica. (c) Azimuthal scan of CdS (1013) ($2\theta = 47.7^{\circ}$, $\chi = 32^{\circ}$) with respect to NaCl (111) ($2\theta = 27.5^{\circ}$, $\chi = 55^{\circ}$) of the 120 nm CdS film on NaCl. (d) Epitaxial lattice alignment of CdS (red) on mica (green) and possible corresponding atomic model. (e) Epitaxial lattice alignment of CdS (red) on NaCl (blue) and possible corresponding atomic model.

CdS in the wurtzite phase was first characterized to establish a reference. The bulk crystal was positioned with its [0001] axis parallel to the direction of laser propagation. For bulk CdS, the frequency of the phonon mode is the real part of phonon self-energy and can be expressed as

$$\omega_{bulk}(T) = \omega_0 + \Delta \omega_e(T) + \Delta \omega_d(T), \tag{1}$$

where ω_0 is the frequency of an optical mode in a perfect harmonic crystal lattice at T = 0 K, $\Delta \omega_e(T)$ is the frequency shift contributed by thermal expansion, and $\Delta \omega_d(T)$ is the frequency shift contribution due to anharmonic coupling or decay of phonons.^{18–20} The term $\Delta \omega_e(T)$ is given by

$$\Delta \omega_e(T) = \omega_0 \left\{ \exp\left[-\gamma \int_0^T \alpha_{\parallel}(T') + 2\alpha_{\perp}(T')dT'\right] - 1 \right\},\tag{2}$$



FIG. 2. Room temperature Raman spectra ($\lambda_{ex} = 514 \text{ nm}$) of CdS with various thicknesses on mica. Inset: an AFM image of 6 nm CdS on mica; RMS roughness is 2.5 nm.

where γ is the Gruneisen parameter for a certain phonon mode of CdS, and $\alpha_{\parallel}(T)$ and $\alpha_{\perp}(T)$ the linear coefficients of thermal expansion (CTE) parallel and perpendicular to the *c*-axis of wurtzite CdS. For the LO mode of CdS, γ is 1.1.²¹ The temperature dependent $\alpha_{\parallel}(T)$ and $\alpha_{\perp}(T)$, in units of K^{-1} , are obtained from a handbook.²² Between 77 K and RT, they can be fitted using Eqs. (S1) and (S2). For term $\Delta \omega_d(T)$, we only considered symmetric decay of zone-center phonons into two (third order) and three phonons (fourth order) with frequencies of $\frac{\omega_0}{2}$ and $\frac{\omega_0}{3}$, respectively; thus, $\Delta \omega_d(T)$ can be written as

$$\Delta \omega_d(T) = M_1 \left[1 + \frac{2}{\exp\left(\frac{\hbar\omega_0}{2k_B T}\right) - 1} \right] + M_2 \left[1 + \frac{3}{\exp\left(\frac{\hbar\omega_0}{3k_B T}\right) - 1} + \frac{3}{\left(\exp\left(\frac{\hbar\omega_0}{3k_B T}\right) - 1\right)^2} \right], \quad (3)$$

where M_1 and M_2 are constants. Substituting Eqs. (2) and (3) into Eq. (1), the experimental temperature dependence of bulk CdS LO phonon frequency can be fitted with $\omega_0 = 305.3 \text{ cm}^{-1}$, $M_1 = -0.0549 \text{ cm}^{-1}$, and $M_2 = -0.0045 \text{ cm}^{-1}$, respectively. Figure 3(a) shows the fitting, along with the individual contribution from thermal expansion, third order, and fourth order phonon decay. One can see that the major contribution to $\omega_{bulk}(T)$ is from the anharmonic coupling, and the thermal expansion plays a minor role.

The reference of a bulk single crystal CdS was used as the baseline for film investigation. For films, the strain counts as an additional factor to the shift of phonon frequency. Possible sources for strain in films are deposition strain ε_{dep} ,



FIG. 3. (a) The LO phonon frequency of a bulk CdS single crystal as a function of temperature. (b) The LO phonon frequencies of CdS films on mica as a function of temperature, with that of the bulk as a reference. (c) The LO phonon frequency of a 120 nm CdS film on NaCl as a function of temperature, with those of the bulk and 120 nm CdS on mica as references. (d) The LO phonon linewidths of CdS bulk and films on mica as a function of temperature. The circles marking the turning points of change tendency for films.

epitaxial strain ε_{epi} , and thermal strain $\varepsilon_{th}(T)$. ε_{dep} is the strain within the bulk of films developed during deposition due to the non-equilibrium growth condition. ε_{epi} is the film-substrate interface strain due to the misfit of two lattices. $\varepsilon_{th}(T)$ is caused by the difference in CTE of the film and substrate when they are subject to a temperature change. ε_{dep} and ε_{epi} are already set when films finish growth and not expected to change with temperature, but $\varepsilon_{th}(T)$ is and given by

$$\varepsilon_{th}(T) = (1 + \varepsilon_r) \frac{1 + \int_{T_0}^{T} \alpha_{sub} dT'}{1 + \int_{T_0}^{T} \alpha_{\perp}(T') dT'} - 1, \qquad (4)$$

where ε_r is the initial thermal strain resulting from postdeposition cooling from deposition temperature to RT, T_0 is RT, and α_{sub} is the in-plane CTE of substrates. Since CdS deposition was done nearly at T_0 , ε_r can be neglected. The CTE of mica is taken as a constant of $6 \times 10^{-6} \text{ K}^{-1}$.²³ Generally, to convert strain in the wurtzite (0001) plane into shift of phonon frequency, Eq. (5) can be used

$$\Delta\omega = 2\left(a - b\frac{C_{13}}{C_{33}}\right)\varepsilon,\tag{5}$$

where *a* and *b* are the phonon deformation potentials, and C_{13} and C_{33} are the stiffness constants.¹⁹ From references,^{24,25}

 $a = -235 \text{ cm}^{-1}$, $b = -330 \text{ cm}^{-1}$ per unit strain (1%), $C_{13} = 48 \text{ GPa}$, and $C_{33} = 113 \text{ GPa}$ are found for wurtzite CdS. Next, the phonon frequency of CdS films as a function of temperature can be modeled as

$$\omega_{film}(T) = \omega_{bulk}(T) + \Delta \omega_s(T), \tag{6}$$

where $\Delta \omega_s$ is the frequency shift caused by strain. As shown in Fig. 3(b), the frequencies of the LO phonon mode for films are different from that of the bulk and vary among films, suggesting different strain behaviors in these films. Starting with the 120 nm film, it can be seen that at RT, the film is tensile stressed, characterized with a $\Delta \omega = -1 \text{ cm}^{-1}$ or 0.5% strain using Eq. (5). At this thickness, the film has to be relaxed from the interface epitaxial strain ($\varepsilon_{epi} = 0$). The strain likely comes from the deposition process. In addition, Fig. 3(b) shows that the difference in LO phonon frequency between bulk and 120 nm CdS remains unchanged with decreasing temperature, meaning $\varepsilon_{th}(T) = 0$. It implies that the strain in this film is purely ε_{dep} and there is not much interface interaction between the film and the substrate. Mathematically, the phonon frequency of the 120 nm film can be expressed as

$$\omega_{120}(T) = \omega_{bulk}(T) + 2\left(a - b\frac{C_{13}}{C_{33}}\right)\varepsilon_{dep}.$$
(7)

For the 30 nm film, its initial state at RT is similar to that of the 120 nm film ($\varepsilon_{dep} = 0.5\%$) and the ε_{epi} can also be

assumed relieved at this thickness, but this film changes slightly differently with temperature, compared to the 120 nm film. To fit this film, $\varepsilon_{th}(T)$ needs to be taken into account, but not at the full scale yet, because Eq. (4) describes a fully locked interface so that the film and substrate expand (compress) as a single component. If the interface lock is partial, however, a pre-factor ($0 \le \eta \le 1$) needs to be inserted. Essentially, η equals zero for the 120 nm film. For this 30 nm film, we have

$$\omega_{30}(T) = \omega_{bulk}(T) + 2\left(a - b\frac{C_{13}}{C_{33}}\right) \left[\varepsilon_{dep} + \eta\varepsilon_{th}(T)\right]. \tag{8}$$

The fitting using Eq. (8) gives rise to $\eta = 0.6$, meaning that there is non-zero contribution from the interface during temperature change. Still, in Fig. 3(b), the phonon frequency for the 6 nm film is found dissimilar from those of the 30 and 120 nm films. First, the standard deviation is large, due to the low intensity and large linewidth of Raman peaks. The reason will be discussed when analyzing the linewidth. Second, the phonon frequency for this film is almost identical to that of bulk CdS at RT. This suggests that ε_{dep} and ε_{epi} cancel out each other at RT. On the one hand, ε_{epi} is expected to be non-zero at this thickness due to the constrained interface. Given the epitaxial alignment and lattice constants of CdS $(d_{(2\overline{110})} = 4.136 \text{ Å})$ and mica $(d_{(100)} = 5.192 \text{ Å})$, the most probable superlattice at the interface is every 5 CdS unit cells lying on 4 mica unit cells, which will lead to $\varepsilon_{epi} = 0.4\%$ in tensile. On the other hand, ε_{dep} is known to be compressive at the very early stage of film growth. Thus, it is likely that ε_{dep} is similar in magnitude to ε_{epi} , but they compensate each other since they are opposite in sign, leaving a strain-free state at RT. To fit this film, we have

$$\omega_6(T) = \omega_{bulk}(T) + 2\left(a - b\frac{C_{13}}{C_{33}}\right) \left[\varepsilon_{dep} + \varepsilon_{epi} + \eta\varepsilon_{th}(T)\right],\tag{9}$$

where η has to reach the maximum for a reasonable fit, suggesting a large magnitude of locking strength at the CdSmica interface. While experimental data contain a couple of outliers for this film, there is no clear sign of interface relaxation at any temperature. The largest strain resulting from thermal mismatch at the interface, occurring at T = 97 K for this film, can be quantified as $\varepsilon_{th} = -0.4\%$. Along with $\varepsilon_{epi} = 0.4\%$ in tensile in this film, it can be concluded that the vdW interface between CdS and mica can withstand at least 0.4% strain in CdS in either direction without relaxation. A strain of 0.4% may sound small, but it is significant enough for certain applications. For instance, a strain of 0.1% in CdS has been shown to increase its pyroelectric coefficient more than 10 times.⁵ Also, note that this 0.4% strain is from a 6 nm film. With the relation of strain and thickness (see supplementary material), $\varepsilon \propto \frac{1}{\sqrt{t}}$, where *t* is the thickness, it is estimated that a strain of 1.2% can be achieved if CdS is two-monolayer thick (6.7 Å). This gives a sense of how significantly strain engineering could play in layered materials which are mostly thinner than 1 nm.

To reveal how the interface of vdWE differs from that of chemical epitaxy, a 120 nm CdS film on a NaCl(100) substrate was studied using the same deposition and characterization method. The XRD $\omega - 2\theta$ and azimuthal scans in Figs. 1(a) and 1(c) show that the film is in the wurtzite phase and epitaxially aligned with NaCl as shown in Fig. 1(e). The alignment is consistent with that reported in the literature,¹⁶ with only one difference that the CdS film in this study consists of two in-plane twin domains offset 30° to each other in the azimuthal direction (a total of 12 peaks, instead of 6 in theory, observed in Fig. 1(c). Figure 3(c) shows the LO phonon frequency of this film as a function of temperature, along with those of the bulk and 120 nm film on mica for comparison. It is seen that the film starts with a larger strain of $\sim 0.9\%$ in tensile. If the deposition strain is assumed to be non-specific to the substrate and given $\sim 0.5\%$ in the case of 120 nm CdS on mica, an additional strain of ~0.4% must come from the interface for this film. As the temperature decreases, a similar equation to Eq. (9) is used to fit the experimental data. The CTE of NaCl is taken as $38 \times 10^{-6} \text{ K}^{-1}$.²⁶ The larger changing rate for CdS-NaCl in Fig. 3(c) is partially caused by the larger CTE of NaCl compared to that of mica, but there is also a stronger interaction from the interface of CdS-NaCl as evident with $\eta = 0.7$ obtained from the fitting. The sharp contrast in phonon frequency between 120 nm CdS films on mica and NaCl, including initial state and changing rate with temperature, suggests considerably different interfaces of CdS-mica and CdS-NaCl.

Last, the linewidth of the CdS LO phonon was investigated. Figure 3(d) shows its temperature dependence for bulk and films on mica. At any temperature, the linewidth is larger for films compared to bulk, and the thinner the film, the larger the linewidth. The peak broadening is likely caused by the common defects of films, such as crystal mosaicity, surface strain, dislocations, and stacking faults.^{27,28} The presence of defects in films modifies the periodicity of lattice and therefore alters the optical phonon frequency, resulting in a larger dispersion in energy. Phonon confinement, often used to explain the peak broadening, is inapplicable here, since asymmetricity in the peak line shape, a signature of phonon confinement, is not observed.^{29,30} Given that the linewidth represents phonon damping arising from the decay of phonons into lower energetic ones, a model concerning phonon decay processes was used to interpret the change tendency with temperature, given by

$$\Gamma(T) = \Gamma_0 + N_1 \left[1 + \frac{2}{\exp\left(\frac{\hbar\omega_0}{2k_BT}\right) - 1} \right] + N_2 \left[1 + \frac{3}{\exp\left(\frac{\hbar\omega_0}{3k_BT}\right) - 1} + \frac{3}{\left(\exp\left(\frac{\hbar\omega_0}{3k_BT}\right) - 1\right)^2} \right],$$
(10)

where Γ_0 is the linewidth at T = 0 K and N_1 and N_2 are constants.¹⁹ Using Eq. (10), the bulk CdS can be well-described with $\Gamma_0 = 4.1 \text{ cm}^{-1}$, $N_1 = 0.105 \text{ cm}^{-1}$, and $N_2 = 0.005 \text{ cm}^{-1}$. However, Eq. (10) cannot be used for films in this work, as there is a turning point around 200–300 K for films, marked

in Fig. 3(d). This abnormality is hypothesized to be related to certain defects such as internal local strain at the grain boundary, which could become significantly dominant at low temperature.³¹

To conclude, this study probed the elastic strain at the interface of 3D-2D vdW heterostructures using a case study of CdS-mica. The interface strain induced by temperature was monitored by Raman spectroscopy. For relatively thick films, the vdW interface was found to be strain-free as expected. However, it was observed that the commonly perceived weak vdW interface can bare at least 0.4% strain in a 6 nm CdS-mica case. Furthermore, an estimation on atomically thin CdS, i.e., two-monolayer, suggests that a strain of 1.2% can be achieved, hinting a good chance of obtaining a significant vdW strain from 2D or sufficiently thin 3D materials. This may expand the benefits of strain engineering in traditional chemical epitaxy to vdWE systems. Lastly, a very different linewidth changing trend of phonon scattering for CdS films was found, which could be a reflectance of defect behaviors in ultrathin films.

See supplementary material for experimental method, fitting equations for CTE of CdS, and relation between interface strain and film thickness.

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