Optical investigation of the natural electron doping in thin MoS$_2$ films deposited on dielectric substrates

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Two-dimensional (2D) compounds provide unique building blocks for novel layered devices and hybrid photonic structures. However, large surface-to-volume ratio in thin films enhances the significance of surface interactions and charging effects requiring new understanding. Here we use micro-photoluminescence (PL) and ultrasonic force microscopy to explore the influence of the dielectric environment on optical properties of a few monolayer MoS$_2$ films. PL spectra for MoS$_2$ films deposited on SiO$_2$ substrates are found to vary widely. This film-to-film variation is suppressed by additional capping of MoS$_2$ with SiO$_2$ and Si$_x$N$_y$, improving mechanical coupling of MoS$_2$ with surrounding dielectrics. We show that the observed PL non-uniformities are related to strong variation in the local electron charging of MoS$_2$ films. In completely encapsulated films, negative charging is enhanced leading to uniform optical properties. Observed great sensitivity of optical characteristics of 2D films to surface interactions has important implications for optoelectronics applications of layered materials.
trion. By comparison with recent work where MoS₂ films were controllably charged by applying voltage⁴, we estimate that observed charging lead to electron densities of the order of 10¹² cm⁻².

**Results**

**PL of thin MoS₂ films.** We carry out low-temperature PL spectroscopy on a wide range of MoS₂ films having thicknesses between 2 and 5 ML, as estimated from the careful colour-contrast examination using optical microscopy, and further confirmed for some films from AFM measurement (see Methods for description of sample fabrication and PL techniques). Fig. 1(a) shows a selection of PL spectra measured for uncapped MoS₂ films deposited on Si substrates with either PECVD (a–d) or thermal oxidation (e–h). In all spectra exciton complexes A and B are clearly visible, although there is a large variation in PL lineshapes for different films. The A complex is composed of a trion PL peak A− and a high energy shoulder A⁰ corresponding to neutral exciton PL⁵. A low energy shoulder L is also observed in some spectra, though spectra showing weak or no contributions of L and A⁰ states were observed on both PECVD (a) and thermal oxide (e) substrates. A relatively large contribution of L and A⁰ was found in many films deposited on PECVD substrates (b, c) and in some cases the neutral exciton was found to have brighter emission than the trion [as in (d)]. For films deposited on thermal oxide substrates, there is a less significant variation in the lineshape (e–h), and L and A⁰ features are, in general, less pronounced relative to A− than in films deposited on PECVD grown SiO₂.

The effect of additional capping of MoS₂ films with dielectric layers is demonstrated in Fig. 2. A 100 nm thick layer of either SiO₂ or Si₃N₄ is deposited using PECVD on top of the MoS₂/SiO₂/Si samples for both PECVD and thermal SiO₂/Si substrates. Here we observe even less variation in lineshapes between the films. A further suppression of the low energy shoulder L and neutral exciton peak A⁰ is found for films capped with Si₃N₄ (a,b,e,f) on both types of substrates, and with SiO₂ on thermally grown substrates. In contrast, L and A⁰ peaks are pronounced when capping with SiO₂ is used for MoS₂ films on PECVD substrates. Further to this, from comparison of spectra in (a,b,c,d) and (e,f,g,h), we find that the PL linewidths of films deposited on the PECVD oxide are notably broader than for those on the thermal oxide substrates.

An interesting trend in all spectra presented in Figs. 1 and 2 is a correlation between the intensities of the features L and A⁰: the two peaks are either both rather pronounced or suppressed in any given spectrum relative to the trion peak A−. This may imply that peak L becomes suppressed when the film captures an excess of negative charge.

**Analysis of PL peak energies.** A statistical analysis of PL peak energies for films deposited on the two types of substrates is presented in Fig. 3. Fig. 3(a,b) show that the average values for the PL peak energies, Eav max for uncapped films are Eav max = 1.888 eV for the PECVD substrates and Eav max = 1.880 eV for thermal oxide substrates, with an almost two times larger standard deviation, σE max for the former (18 versus 11 meV). The data collected for the capped films (shaded for Si₃N₄ and hatched for SiO₂) are presented in Fig. 3(c) and (d) for the thermal and PECVD oxide substrates, respectively. Significant narrowing of the peak energy distribution is found in all cases: σE max = 6 meV has been found. The average peak energies are very similar for both SiO₂ and Si₃N₄ capping on the thermal oxide substrates (Eav max = 1.874 eV), but differ for PECVD substrates: Eav max = 1.862 and 1.870 eV for SiO₂ and Si₃N₄ capping, respectively.

From previous reports, for films with thicknesses in the range 2 to 5 MLs, one can expect the PL peak shift on the order of 20 meV. In addition, PL yield was reported to be about 10 times higher for 2 ML films compared with 4 ML and for 3 ML compared with 5 ML. In our study, the integrated PL signal shows a large variation within about one order of magnitude between the films. The dependence of the PL yield on the type of the substrate and capping is not very pronounced. While our data for PL intensities is consistent with the reported in the literature for the range of thicknesses which we studied, the PL peak energy distribution shows the unexpected
broadening for uncapped samples: for example, deviations from $E_{\text{av}}^{\text{max}}$ by $\pm 20–30$ meV are evident in Fig. 3(a,b). For the capped samples, new trends are observed: the significant narrowing and red-shift of $E_{\text{max}}$. As shown below, these effects reflect changes in the PL lineshapes between the capped and uncapped samples, which in turn reflect changes in the relative intensities of the $A^-$, $A^0$ and $L$ peaks.

We note that the new experimental trends observed in our PL studies do not depend on the exact distribution of thicknesses in the ensembles of the investigated films, provided these distributions are similar for all types of samples studied. The latter is the case in our study, as the films were produced using the same method, show similar range of the colour-contrasts under optical examination, and exhibit similar ranges of PL yield.

**Analysis of PL lineshapes.** In this section we will present the lineshape analysis for the $A$ exciton PL based on the measurement of full width at half maximum (FWHM) in each PL spectrum. This approach allows one to account for contributions of the three PL features, $L$, $A^0$ and $A^-$. The data are summarized in Fig. 4 and Table 1.

**PECVD grown SiO$_2$ substrates.** These data are presented in Fig. 4 in red. Data for uncapped films are shown in Fig. 4(a), from where it is evident that the lineshapes vary dramatically from film to film within a range from 50 to 170 meV. FWHM for uncapped films on PECVD grown substrates is on average $\Delta E_{\text{FWHM}} \approx 96$ with a large standard deviation $\sigma_{\text{FWHM}} = 33$ meV. This gives a rather high coefficient of variation $\sigma_{\text{FWHM}}/\Delta E_{\text{FWHM}} \approx 0.34$.

The non-uniformity of lineshapes of the PL spectra is significantly suppressed by capping the films with Si$_x$N$_y$ and SiO$_2$ (shown with red in Fig. 4(b) and (c), respectively). This is evidenced from the reduction of the coefficient of variation in the FWHM values by a factor of 4 in capped films compared with the uncapped samples (in Table 1). Despite the narrowed spread of $\Delta E_{\text{FWHM}}$ values, the average FWHM are similar for all types of samples studied. The latter is the case in our study, as the films were produced using the same method, show similar range of the colour-contrasts under optical examination, and exhibit similar ranges of PL yield.

**Table 1 | Mean values, standard deviations and coefficients of variation for full width at half maximum of PL spectra measured for thin MoS$_2$ films**

| Substrate/Capping | Mean value (meV) | Standard deviation (meV) | Coefficient of variation |
|-------------------|------------------|--------------------------|-------------------------|
| PECVD/uncapped    | 96               | 33                       | 0.34                    |
| PECVD/SiO$_2$     | 109              | 9                        | 0.08                    |
| PECVD/Si$_x$N$_y$ | 84               | 7                        | 0.08                    |
| Thermal/uncapped  | 79               | 12                       | 0.15                    |
| Thermal/SiO$_2$   | 76               | 7                        | 0.09                    |
| Thermal/Si$_x$N$_y$ | 64            | 4                        | 0.06                    |

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Figure 3 | (a–d) PL peak energies for $A$ exciton complex in MoS$_2$ thin films. Data for films deposited on thermally (PECVD) grown SiO$_2$ substrates are shown in top (bottom) panels. Panels (a)–(b) and (c)–(d) show PL peak positions for uncapped and capped films, respectively.

Figure 4 | PL FWHM of exciton complex $A$ in thin MoS$_2$ films. Data for MoS$_2$ films deposited on thermally and PECVD grown SiO$_2$ substrates is shown with blue and red, respectively. (a) PL FWHM of uncapped MoS$_2$ films. (b) PL FWHM of Si$_x$N$_y$ capped MoS$_2$ films. (c) PL FWHM of SiO$_2$ capped MoS$_2$ films.
in SiO2 capped films is rather high, 109 meV, which reflects relatively strong contribution of L and $A^0$ PL features. Contributions of $A^+$, L and $A^+$ features vary very considerably in the uncapped samples, leading to an average smaller linewidths but a very significant spread in FWHM values. In contrast, in Si$_3$N$_4$ capped films, $A^+$ peak dominates and both L and $A^+$ features are relatively weak, which effectively results in narrowing of PL.

**Thermally grown SiO2 substrates.** These data are presented in Fig. 4 in blue. It can be seen that uncapped films deposited on the flatter thermal oxide substrates appear to have significantly narrower distributions of linewidths compared to uncapped films on PECVD substrates: coefficient of variation of $\Delta E_{\text{FWHM}}$ is by a factor of 2 smaller for films on the thermally grown substrates [see Fig. 4(a) and Table 1]. In addition, compared with the films deposited on PECVD grown SiO2, FWHM is also reduced by about 20% to 79 meV. Such narrowing reflects weaker contribution of L and $A^0$ peaks in PL spectra.

The non-uniformity of the PL spectra still present in uncapped films deposited on thermally grown SiO2 is further suppressed by capping the films with Si$_3$N$_4$ and SiO2 [shown with blue in Fig. 4(b) and (c), respectively]. In general, the coefficients of variation for FWHM of the capped films are rather similar for both substrates and are in the range of 0.06–0.09, showing significant improvement of the reproducibility of PL features compared with the uncapped samples (see Table 1). For Si$_3$N$_4$ capped films on thermally grown SiO2, we also observe narrowing of PL emission to $\Delta E_{\text{FWHM}} = 64$ meV. This reflects further suppression of L and $A^0$ relative to $A^+$, the effect less pronounced in SiO2 capped films.

**AFM and UFM measurements.** To further understand the interactions between MoS2 films and the substrate/capping materials, we carried out detailed AFM and UFM measurements of our samples (Fig. 5). AFM measurements of films deposited on PECVD grown substrates Fig. 5(a) show that the film is distorted in shape and follows the morphology of the underlying substrate. The root mean square (rms) roughness $R_{\text{rms}}$ of these films is 1.7 nm with a maximum height $R_{\text{max}} = 11$ nm, similar to the parameters of the substrate, $R_{\text{rms}} = 2$ nm and $R_{\text{max}} = 15$ nm. Such $R_{\text{max}}$ is greater than the thickness of films (<3 nm), leading to significant film distortions. UFM measurements of these films [Fig. 5(b)] show small areas of higher stiffness (light colour, marked with arrows) and much larger areas of low stiffness (i.e. no contact with the substrate) shown with a dark colour. This shows that the film is largely suspended above the substrate on point contacts.

AFM measurements of films deposited on thermally grown SiO2 substrates [Fig. 5(c)] show a much more uniform film surface due to the less rough underlying substrate. This is reflected in a significantly improved $R_{\text{rms}} = 0.3$ nm and $R_{\text{max}} = 1.8$ nm. These values are still higher than those for the bare substrate with $R_{\text{rms}} = 0.09$ nm and $R_{\text{max}} = 0.68$ nm. A more uniform stiffness distribution is observed for these films in UFM [Fig. 5(d)], although the darker colour of the film demonstrates that it is much softer than the surrounding substrate and thus still has relatively poor contact with the substrate. A darker shading at film edges demonstrates that they have poorer contact than the film center and effectively curl away from the substrate.

AFM and UFM data for films capped with 15 nm SiO2 after deposition on PECVD and thermally grown SiO2 are given in Fig. 5(e, f) and (g, h), respectively. For the PECVD substrate, the roughness of the MoS2 film is similar to that in the uncapped sample in Fig. 5(a): $R_{\text{rms}} = 1.68$ nm and $R_{\text{max}} = 10.2$ nm. From the UFM data in Fig. 5(f), it is evident that although the contact of the MoS2 film with the surrounding SiO2 is greatly improved compared with the uncapped films, a large degree of non-uniformity is still present, as concluded from many dark spots on the UFM image. In great contrast to that, the capped MoS2 film on thermally grown SiO2 is flatter [Fig. 5(g, h)], $R_{\text{rms}} = 0.42$ nm and $R_{\text{max}} = 6.1$ nm, with the roughness most likely originating from the PECVD grown SiO2 capping layer. The UFM image in Fig. 5(h) shows remarkable uniformity of the stiffness of the film similar to that of the capped substrate, demonstrating uniform and firm contact (i.e. improved mechanical coupling) between the MoS2 film and the surrounding dielectrics.

**Discussion**

There is a marked correlation between the PL properties of the MoS2 films and film stiffness measured by UFM. The stiffness reflects the strength of the mechanical coupling between the adjacent monolayers of the MoS2 film and the surrounding dielectrics. The increased bonding and its uniformity for films deposited on less rough thermally grown SiO2 substrates and for capped MoS2 films manifests in the more reproducible PL characteristics, leading to reduced standard deviations of the peak positions and linewidths. These spectral characteristics are influenced by the relative intensities of the three dominating PL features, trion $A^+$, neutral exciton $A^0$ and low energy L peak, which are influenced by the charge balance in the MoS2 films sensitive to the dielectric environment. The efficiency of charging can be qualitatively estimated from the relative intensities of $A^+$ and $A^0$ peaks. In the vast majority of the films, $A^+$ dominates. As noted above, the intensity of $A^+$ directly correlates (qualitatively) with that of the relatively broad low energy PL shoulder L (see Fig. 1 and 2), previously ascribed to emission from surface states. The line-
shape analysis presented in Fig. 4 and Table 1 is particularly sensitive to the contribution of peak L.

The PL lineshape analysis and comparison with the UFM data lead to conclusion that negative charging of the MoS2 films is relatively inefficient for partly suspended uncapped films on rough PECVD substrates. Both in SiO2 and SiNx capped films on PECVD substrates, the charging effects are more pronounced. However, both A’ and L features still have rather high intensities. The relatively low charging efficiency is most likely related to a non-uniform bonding between the MoS2 films and the surrounding dielectric layers as concluded from from UFM data [see Fig. 5(0)]. The charging is more pronounced for uncapped MoS2 films on thermal oxide substrates, and is enhanced significantly more for capped films: for SiNx, capping A’ and L peaks only appear as weak shoulders in PL spectra.

It is clear from this analysis that the charge balance in the MoS2 films is altered strongly when the films are brought in close and uniform contact with the surrounding dielectrics, enabling efficient transfer of charge in a monolithic hybrid heterostructure. Both n-type10,15 and p-type17,18 conductivities have been reported in thin MoS2 films deposited on SiO2. It is thus possible that the sign and density of charges in exfoliated MoS2 films may be strongly affected by the properties of PECVD grown SiO2 and SiNx, where the electronic properties may vary depending on the growth conditions19–21.

It is notable, however, that for a large variety of samples studied in this work, the negative charge accumulation in the MoS2 films is pronounced, and is further enhanced when the bonding of the films with the dielectric layers is improved.

In order to estimate the density of the accumulated charges we refer to Ref. 16, where PL spectra as a function of electron density in the film were measured. The neutral exciton PL peak A’ becomes less intense than the trion peak A’’ at the electron density n = 2 × 1014 cm⁻². Since in our experiments in many films A’ peak is relatively pronounced, we conclude that we have studied the regime where the electron densities are of the order of 10¹³ cm⁻² or less.

The band-structure of MoS2 and hence its optical characteristics can also be influenced by strain22–24. However, the distribution and magnitude of strain cannot be assessed directly in our experiments. The variation of PL spectral lineshapes, neutral exciton peak A’’ relative to the contribution of peak L, and Table 1 is particularly sensitive to the resonance frequencies of the AFM cantilever. The resulting sample stress produces a reaction, that is modified by the voids, subsurface defects or sample-independent of the substrate type, the uncapped thin MoS2 films had optical contrasts corresponding to thicknesses of 2–5 MÅ, further confirmed by AFM on thermal oxide substrates. Furthermore, the range of PL yield was similar for all four types of sample independent of the substrate and capping type, further indicating that ensembles of films with similar distributions of film thicknesses were measured.

Methods

Sample preparation. MoS2 was exfoliated using the mechanical cleavage method1 and deposited on commercially purchased Si wafers with a low roughness 300 nm thick thermally grown SiO2. Further MoS2 samples were produced using the same technique, but deposited on Si substrates covered with 300 nm PECVD grown SiO2. PECVD deposition was done in a 60 °C chamber with a sample temperature of 300 °C. The root mean square (rms) roughness, Rrms, of the thermally grown SiO2 is found to be 2 nm with a maximum peak height of 15 nm, whereas Rrms, of the thermally grown SiO2 Si samples with SiNx and SiNx were carried out using the same PECVD techniques. The complete SiO2/MoS2/SiO2/Si or SiNx/MoS2/SiO2/Si samples had the top SiN, and SiO2 layers with thicknesses of 100 nm for PL and 15 nm for AFM/UFM measurements. The high surface roughness rendered impractical use of AFM for measurements of the film thicknesses on PECVD substrates. However, independent of the substrate type, the uncapped thin MoS2 films had optical contrasts corresponding to thicknesses of 2–5 MÅ, further confirmed by AFM on thermal oxide substrates. Furthermore, the range of PL yield was similar for all four types of sample independent of the substrate and capping type, further indicating that ensembles of films with similar distributions of film thicknesses were measured.

Micro-photoluminescence experiments. Low temperature (10 K) micro-PL was carried out on a large number of thin films in a continuous flow He cryostat. The signal was collected and analyzed using a single spectrometer and a nitrogen-cooled charged-coupled device. The sample was excited with a laser at 532 nm. All PL spectra presented in this work were measured in a range of low powers where no dependence on power of PL lineshape was found.

AFM/UFM experiments. As shown elsewhere22, the ultrasonic force microscopy (UFM) allows imaging of the near-surface features and subsurface interfaces with superior nanometre scale resolution compared to AFM techniques11. In the sample-UFM modality used in this paper23, the sample in contact with the AFM tip is vibrated at small amplitude (0.5–2 nm) and high frequency (2–10 MHz), much higher than the resonance frequencies of the AFM cantilever. The resulting sample stress produces a reaction, that is modified by the voids, subsurface defects or sample-substrate interfaces, and can be detected as an additional ‘ultrasonic’ force. A unique feature of UFM is that it enables nanometre scale resolution imaging of morphology of subsurface nano-structures and interfaces of solid-state objects. In order to interpret the images of a few layer films presented in Fig. 5, one can note that the bright (dark) colors correspond to higher (lower) sample stiffness.

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