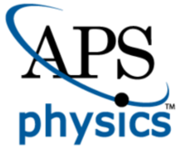

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Imaging Atomically Thin Semiconductors Beneath Dielectrics via Deep Ultraviolet Photoemission Electron Microscopy

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Sub-surface imaging of atomically-thin semiconductors beneath dielectrics based on optical standing wave using photoemission electron microscopy with deep-ultraviolet photoexcitation

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Imaging of fabricated nano-structures or nano-materials covered by dielectrics is highly sought after for diagnostics of optoelectronics components. We show imaging of atomically-thin MoS_2 flakes grown on SiO_2-covered Si substrates and buried beneath HfO_2 overlayers up to 120 nm in thickness using photoemission electron microscopy with deep-ultraviolet (UV) photoexcitation. Comparison of photoemission yield (PEY) to modelled optical absorption evinced the formation of optical standing waves in the dielectric stacks (i.e., cavity resonances of HfO_2 and SiO_2 layers on Si). The presence of atomically-thin MoS_2 flakes modifies the optical properties of the dielectric stack locally. Accordingly, the cavity resonance condition varies between the sample locations over buried MoS_2 and surrounding areas, resulting in image contrast with submicron lateral resolution. This sub-surface sensitivity underscores the role of optical effects in photoemission imaging with low-energy photons. This approach can be extended to non-destructive imaging of buried interfaces and sub-surface features needed for analysis of microelectronic circuits and nanomaterial integration into optoelectronic devices.

Introduction:

From sonograms to geological surveys, scientists and engineers have searched for accurate and reliable approaches for inspecting internal or “buried” structures non-destructively. For micro- and nano-electronic devices, the challenge has been to achieve microscopy of buried interfaces and sub-surface features, which are often encapsulated within dielectric or insulating films.[1,2] To that end, numerous microscopy techniques have been applied, including: optical microscopy,[1] imaging ellipsometry,[3] scanning and transmission electron microscopies,[4,5,6,7,8,9] and, more recently, scanning probe microscopy,[2,10,11,12] x-ray microscopy,[13,14] and photoemission electron microscopy (PEEM).[15,16] There are three criteria by which successful internal imaging is gauged: spatial resolution down to the nanometer scale, depth sensitivity, and non-destructiveness. Thus far, satisfying all three requirements simultaneously remains elusive.

Of these techniques, PEEM remains promising due to its high depth sensitivity[17] via two known characteristics of photoemission processes: (1) optical standing waves typically formed when using medium- to high-energy photons (x-rays),[18,19,20,21,22] and (2) longer photoelectron mean free paths achievable with photoexcitation using high- or very low-energy photons as opposed to medium-energy photons (we specify the photon's energy range in ref. 23).[24,25,26,27,28] Both approaches can stimulate the photoelectron emission from sub-surface regions of the sample. Due to sample charging, dielectrics are excluded from the use of medium- to high-energy photons in photoemission measurement in general. To allow for imaging of samples covered with dielectrics with enhanced depth sensitivity,[29,30] we therefore sought to exploit the PEEM imaging with low-energy photons, which can establish optical standing waves[31,32] or generate low-kinetic-energy photoelectrons with anticipated longer mean free paths.[7,33] In this work, we demonstrate sub-surface imaging based on PEEM using deep-ultraviolet (deep-UV) excitation. The optical standing waves formed by deep-UV photons have enabled imaging of atomically-thin MoS_2 flakes beneath HfO_2 films up to a 120 nm-thick. This sample structure emulates the architecture of general electronics components, in which electrically-active layers are buried under passivating dielectrics. We further confirmed imaging sub-surface features buried beneath two other oxides - Al_2O_3 and SiO_2. Thus, this approach is viable for sub-surface imaging beneath common dielectrics used in microelectronics.

Results:

A. Sub-surface imaging and photon wavelength-dependent image contrast

Using PEEM with low-energy photons, we imaged atomically-thin MoS_2 flakes covered with varying thicknesses of HfO_2 overlayers as shown in Figs. 1 (a) to (j). We chose HfO_2 overlayers because HfO_2 is commonly used in micro- and nanoelectronics owing to its high dielectric constant and has a relatively high refractive index in the UV spectrum. Layers of MoS_2 are only several-atoms thick (each MoS_2 monolayer is three-atoms thick), making detection of buried MoS_2 layers an excellent test of sub-surface sensitivity. Atomically-thin MoS_2 flakes (mostly monolayer specimens, with some multilayer regions near the center of the flakes) were grown on Si wafers covered with 100 nm-thick SiO_2.[34] We then covered the entire sample surface with HfO_2 overlayers via atomic layer deposition (ALD).[35,36,37] Thus, SiO_2 and HfO_2 films encapsulate MoS_2 flakes, as illustrated in Figs. 1 (k) and (l).

Despite being buried, MoS_2 flakes, with their characteristic triangular shape, were visible through the HfO_2 overlayers, ranging in thickness from 0 nm to over 100 nm.[37] Figs. 1 (a) to (d) show clear image contrast between the buried MoS_2 and surrounding areas. In addition, the image contrast changes as a function of the photoexcitation wavelength. Figs. 1 (e) to (j) show one such example of the wavelength-dependence for the 21 nm-thick HfO_2 film.[38] Raman measurement (not shown) confirmed that the small dots near the periphery of MoS_2 flakes are smaller crystallites of MoS_2. We did not encounter sample charging within our detection limit except for the thickest 103 nm-thick HfO_2 overlayer, and only when examined using photons with wavelength below λ = 195 nm. We suppose that the minimal conductivity of dielectrics (presumably due to defects) is still high enough to replenish the relatively small number of

electrons lost during photoemission, when excited by the comparatively low-energy, low-flux photons of DUV-PEEM. The results highlighted in Fig. 1 are similar to photoemission experiments carried out on conductive samples using hard x-rays (i.e., high-energy photons)[28,39], whereas in our case we realized sub-surface imaging through insulating dielectrics with deep-UV photons. The notably large depth sensitivity to buried structures is the key outcome of this work.

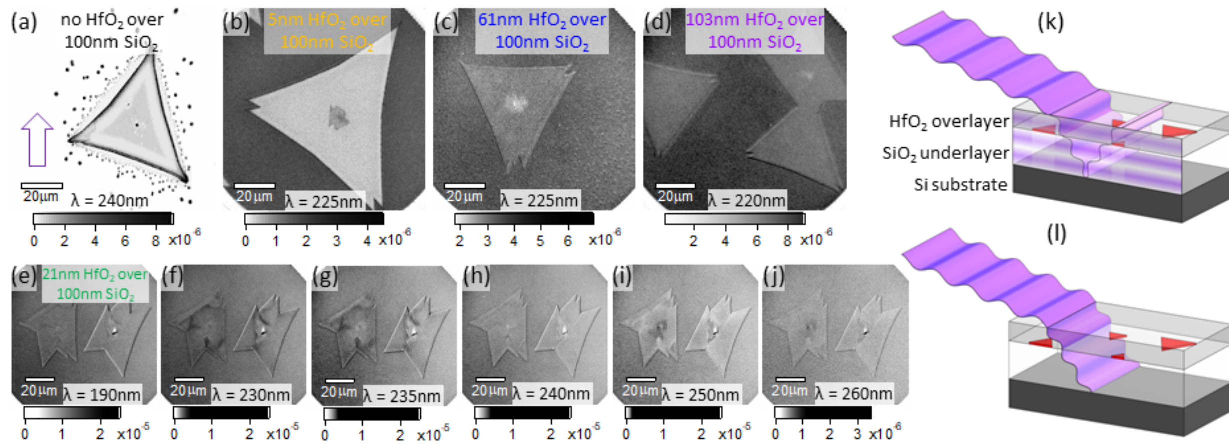

FIG. 1 PEEM images of MoS_2 flakes covered with HfO_2 films on 100 nm-thick SiO_2 underlayers, and illustrations of sample geometry and standing wave formation within the dielectric stack. (a) to (d) show kinetic-energy-integrated photoemission yield (PEY) images (i.e., the photoemission intensity is integrated across the entire electron kinetic energy range, and then converted to the unit of photoemission yield; see ref. 40 for details). The thicknesses of HfO_2 films (0 nm, 5 nm, 61 nm, and 100 nm HfO_2) are labeled at the top of image. (e) to (j) show the photon wavelength-dependence of the kinetic-energy-integrated PEY images for 21 nm-thick HfO_2 overlayer. Scale bars for photoemission yield, shown at the bottom of (a) to (j), represent higher yield as dark grey. The photon wavelength used for these measurements are labeled in each image. The arrow in (a) indicates the in-plane direction of the incident wavevector of deep-UV sample illumination. Purple waves and red triangular islands in (k) and (l) depict deep-UV illumination of buried MoS_2 flakes with an incident angle of 73° off-normal to the sample surface defined by the instrument's geometry. When the deep-UV wavelength matches the cavity's resonance condition, a standing wave forms in the dielectric, as illustrated by the color gradation (purple) in the dielectric films in (k). The non-resonance case is illustrated in (l).

B. Photoemission yield (PEY) and optical absorption modeling

The large depth sensitivity as well as the wavelength-dependent image contrast emerges as a consequence of optical standing waves, which form in the dielectric stacks via deep-UV photon illumination. To support this assertion, we first describe a signature of the optical standing waves by comparing the experimentally-determined photoemission yield (PEY) to the modelled optical absorption within the dielectric stack. We modelled the optical absorption using a transfer matrix approach that captures thin film interference. In Fig. 2 (a), we show the wavelength-dependent PEY measured from samples with varying HfO_2 overlayer thicknesses atop 100 nm-thick SiO_2 underlayers. The definition of the PEY and the measurement protocol is given in refs. 40 and 41, respectively. We obtained PEY spectra

from a series of total photoemission yield images recorded as a function of the photoexcitation wavelength at a given sample location.

Most importantly, PEY spectra exhibited resonance-like peaks shown in Fig. 2 (a), highlighted by open and filled circles. Solid lines in Fig. 2 (a) represent PEY spectra obtained from the area above HfO_2-covered SiO_2 (*without* the MoS_2 flakes). Dotted lines in Fig. 2 (a) are the spectra taken at sample locations over HfO_2-covered MoS_2 flakes on SiO_2. We quantified the wavelength of resonance-like peaks in Fig. 2 (a), denoted by filled circles, by fitting PEY spectra with Gaussian functions superimposed over a polynomial background. Open circles designate peaks that weren't clearly defined, due to relatively low signal-to-noise ratio (therefore, no fitting conducted). Fitting of resonance-like peaks shows a slight shift in peak positions between the dotted and solid lines for samples with HfO_2 thicknesses > 5nm. We discuss the cause and implications of this slight shift in the subsequent section describing Fig. 3. Aside from these peak shifts, PEY spectra are very similar between the sample areas over MoS_2 and SiO_2. For thin HfO_2 overlayers ≤ 5nm, Fig. 2 (a) shows PEY spectra from areas above the MoS_2 flakes and the SiO_2 that were noticeably different, with peaks apparent for SiO_2 areas only. Overall, the PEY spectra exhibited near-exponential increase for shorter photoexcitation wavelengths (i.e., higher photon energy) as reported previously,[42,43] with an abrupt decrease below λ = 190 nm (not shown). This abrupt decrease of the PEY is due to reduced photon flux and hence lower photoemission intensity, owing to poor light transmission by the optics in this wavelength range and the cutoff of the light source. For our setup, we also note that the measurement of light intensity for wavelengths below λ = 200 nm is less accurate than that above λ = 200 nm due to a calibration issue.[40]

We establish that resonance-like peaks in PEY spectra shown in Fig. 2 (a) are signatures of optical standing waves (i.e., cavity resonance of the thin film waveguides) by comparing the peak positions to the modelled optical absorption. In Fig. 2 (b), the grey scale contrast shows the modelled total optical absorption (1 - R) as a function of the photoexcitation wavelength, and HfO_2 overlayer thickness of the dielectric stacks. Higher optical absorption is represented as darker grey. We obtained the total optical absorption using the transfer matrix method to account for light propagation and interference within an optical cavity comprised of a Si substrate, a 100 nm-thick SiO_2 underlayer, and a HfO_2 overlayer. We averaged the s- and p-polarized illuminations to simulate unpolarized light at 73° angle of incidence, consistent with the experimental geometry. Optical parameters used for the model are given in ref. 44.

In Fig. 2 (b), four high-absorption bands (i.e., darker grey bands), which extend from smaller HfO_2 thickness at lower photon wavelength to larger HfO_2 thickness at higher photon wavelength, correspond to optical absorption modes of the dielectric cavity. The positions of resonance-like peaks in PEY spectra from the HfO_2-covered SiO_2 areas without the MoS_2 flakes [circles in Figs. 2 (a) and (b)] match remarkably well with the wavelengths of high optical absorption expected from the model.[45] This result supports the notion of higher PEY due to enhanced light absorption from the formation of optical standing waves within the dielectric stack. Figs. 1 (k) and (l) illustrate the resonance and non-resonance conditions, respectively.[31] Furthermore, the formation of optical standing waves explains the wavelength-dependent changes in image contrast observed between buried MoS_2 flakes and surrounding areas shown in Figs. 1 (e) to (j).[38] Specifically, the image contrast increases at wavelengths near the resonance-like peaks in PEY spectra (e.g., between 230 nm and 250 nm for the 21 nm-thick

HfO_2 film) and is less prominent at other wavelengths. At these resonance wavelengths, the presence of the MoS_2 flakes "de-tuned" the cavity resonance resulting in significant changes in PEY that are observed as image contrast. This "de-tuning" of the resonance is also the origin for the slight shift in the PEY peak shown in Fig. 2 (a) between the locations over MoS_2 flakes and over the surrounding SiO_2 area.

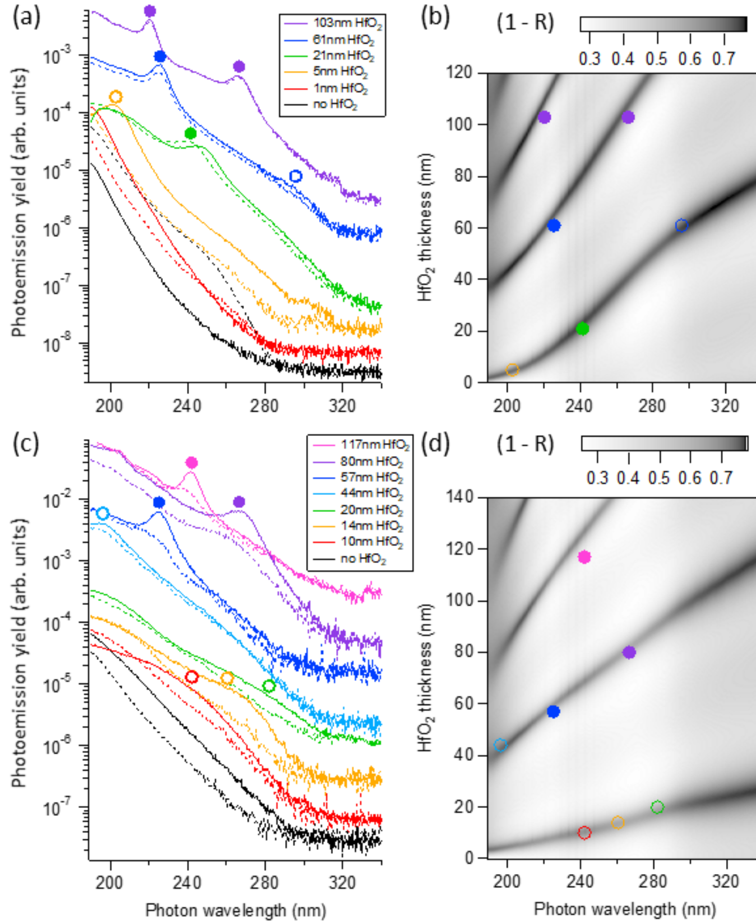

FIG. 2 Photoemission yield (PEY) spectra and the modelled optical absorption of the dielectric cavity. (a) PEY spectra as a function of photon energy obtained at sample locations over MoS_2 flakes (dotted lines) and SiO_2 (solid lines), for dielectric stacks with 100 nm-thick SiO_2 and different HfO_2 overlayer thicknesses. Spectra except for black ones are shifted along the vertical axis for clarity. Filled circles indicate peak positions in PEY spectra, while open circles denote the positions of low-intensity peaks. We determined all peak positions from PEY spectra over SiO_2 (solid lines). (b) Total optical absorption (1-*R*) calculated for dielectric cavities comprised of stacks of HfO_2 films with varying thickness atop 100 nm-thick SiO_2. The filled and open circles overlaid on calculated absorption spectra in (b) depict the positions of resonance peaks in PEY spectra (a). (c) PEY spectra similar to (a) for dielectric stacks with nominally 12 nm-thick SiO_2 and different HfO_2 overlayer thicknesses. Again, spectra except for black ones are shifted along the vertical axis for clarity. (d) Total optical absorption (1-*R*) calculated for dielectric cavities comprised of stacks of HfO_2 films with varying thickness atop 15 nm-thick SiO_2.

We underscored the formation of the optical standing wave by examining PEY spectra from complementary dielectric stacks, in which the SiO_2 underlayer was nominally 12 nm-thick, as opposed to 100 nm-thick SiO_2 discussed thus far. Most of the MoS_2 flakes are monolayer specimens with some coexisting multilayer areas (mostly less than five layers). The 12 nm-thick SiO_2 underlayer resulted inadvertently from the growth of MoS_2 flakes on Si wafers covered with native oxide. The thickness of underlayer SiO_2 was 12 nm estimated using optical ellipsometry.[46]

Fig. 2 (c) shows PEY spectra as a function of the incident photon wavelength for samples having a thinner SiO_2 underlayer, with varying thicknesses of HfO_2 overlayers. Again, the dotted lines of Fig. 2 (c) represent the PEY spectra taken at sample locations over MoS_2 flakes, whereas solid lines represent spectra over the surrounding SiO_2 areas. Similar to the dielectric stacks with 100 nm-thick SiO_2 underlayers, the PEY spectra in Fig. 2 (c) exhibited near-exponential increases toward shorter photoexcitation wavelengths. Importantly, the resonance-like peaks ride atop the near-exponential trend of PEY spectra, highlighted by open and filled circles. This result substantiates the optical standing wave formation in the dielectric stack that is general and not limited to particular dielectric stacks. Differences do exist in the PEY spectra between films of two SiO_2 underlayer thicknesses, however. There is a lack of prominent resonant peaks for all regions in which HfO_2 overlayers are less than ~50 nm. Additionally, we see the suppressed intensity of resonance-like peaks for areas covered by MoS_2 flakes compared to surrounding areas [compare solid and dotted lines of Fig. 2(c)]. This observation contrasts with the dielectric stacks with thicker SiO_2 underlayers [Fig. 2(a)], where the amplitudes of the resonance-like peaks between the two regions are nearly equivalent in magnitude, albeit shifted in wavelength.

For dielectric stacks with nominally 12 nm-thick SiO_2 underlayers, we again tested the formation of the optical standing wave by comparing the peak positions in the PEY spectra to the modelled optical absorption, as shown in Fig. 2 (d). The high optical absorption bands represented as darker grey show remarkable coincidence to the PEY peak positions. We note that the magnitude of the modeled absorption is lower for the dielectrics stacks with the thinner SiO_2 underlayers [Fig. 2 (d)] compared to those with 100 nm-thick SiO_2 underlayers [Fig. 2 (b)]. The reduced absorption is most apparent in the bottom portion of Fig. 2 (d) where the HfO_2 overlayer is thinnest. We postulate that this reduced absorption contributes to the lack of well-established resonance peaks observed in the PEY for sub-50 nm HfO_2 overlayers, shown in Fig. 2(c).

We obtained the best match between the modelled optical absorption and the PEY peak positions by assuming 15 nm-thick SiO_2 underlayers instead of 12 nm, the nominal thickness of SiO_2 underlayers having been derived from optical ellipsometry.[46] We speculate that this discrepancy may be due to the optical properties of the SiO_2 underlayer, different from that of a pure thermal oxide, as well as defective interfaces between thin-film dielectrics and the Si substrate promoted during the ALD growth of HfO_2 overlayers. Defected SiO_2 underlayers could also explain the reduced resonance peak intensity in areas covered by MoS_2 flakes, as defects could result in the absence of a well-defined SiO_2-MoS_2 interface capable of bleeding out the optical wave, partially quenching the resonant effect.[47]

Based on the examinations of two complementary dielectric stacks, we conclude that the resonance-like peaks in the PEY spectra as well as the wavelength-dependent image contrast arise due to the formation of optical standing waves from deep-UV photons used for PEEM imaging. In the UV range, the refractive indices of HfO_2 and SiO_2 are relatively high. Whereas, Si has a low refractive index particularly below the wavelength of 270 nm reaching close to unity around 200 nm. The differences in the refractive indices allow for forming dielectrics cavities particularly for the photons at shorter wavelength. The effect of these standing waves, in turn, provides a means to perform sub-surface PEEM imaging beneath non-conductive dielectric layers.

C. Microscopic analysis of the optical phase contrast

PEEM imaging based on deep-UV standing waves has the potential not only for sub-surface imaging but also for mapping local optical parameters (i.e., the refractive index or high-frequency dielectric function), which dictate the propagation of deep-UV photons. To explain, we first recognize that the resonance of the optical cavity, and thus the PEY, is sensitive to the optical path taken by the deep-UV photons. These photons propagate based on the optical constants of the materials forming the cavity, and the wavelength and incident angle of the light.[18,19,20,21,22] Incorporating atomically-thin MoS_2 flakes alters the propagation of the photons locally, resulting in a change of the optical cavity. This modifies the PEY spectrum's resonant wavelength and total peak area.[48] The resonance-peak wavelength and area, therefore, contain information regarding local optical properties.

Exploiting this notion and the spectroscopic imaging data, we show in Fig. 3 false color maps of the local cavity resonance peaks in terms of wavelength [(a), (c), and (e)] and total peak area [(b), (d), and (f)]. We obtained these false color maps for samples with 21 nm- and 61 nm-thick HfO_2 overlayers on 100 nm-thick SiO_2 underlayers, and for 117 nm-thick HfO_2 on nominally 12 nm-thick SiO_2. Using the three-dimensional dataset of the spectroscopic imaging, we created these images by fitting the PEY spectrum from each pixel in the image, whereupon we assigned a color based on the value of the resonance peak wavelength or the total peak area.

The resulting images provide an impressive level of structural details for the buried MoS_2 flakes, as shown in Fig. 3. Beyond merely exhibiting the expected triangular geometry characteristic of MoS_2 flakes derived from chemical vapor deposition processes,[49] the peak wavelength image [Fig. 3 (a)] indicate that each specimen was comprised of three to four flakes that coalesced and merged during growth. Specifically, the locations of low-wavelength resonance peaks (green areas) coincided with boundaries expected to exist between domains with different crystallographic orientations. The orange to red areas, meanwhile, match the locations where multilayer MoS_2 is expected. Similarly, the total peak area map of Fig. 3 (b) highlights the locations of domain boundaries as well. Unlike peak wavelength images, the left and right sides of MoS_2 flakes appear different in the peak area image in Fig. 3 (b), as highlighted by ovals. We suspect this contrast asymmetry results from the incident light direction [arrow in Fig. 3 (a)] and the consequent light interference as deep-UV photons propagate through areas with encapsulated MoS_2 flakes. We found similar image contrast variation at the boundaries between flakes and multilayer

areas for the sample with the 61 nm-thick [Figs. 3 (c) and (d)] and 103 nm-thick HfO_2 overlayers (not shown) on 100 nm-thick SiO_2 underlayer. Although less clearly resolved, the sample with 117 nm-thick HfO_2 on nominally 12 nm-thick SiO_2 underlayer also displays the triangular geometry of buried MoS_2 flakes in both resonant peak wavelength and the total peak area images [Figs. 3 (e) and (f)], as well as contrast asymmetry highlighted by ovals in the total peak area image [Fig. 3 (f)].

Spectroscopic imaging of the standing wave resonances demonstrates its outstanding sensitivity to the structural details of the buried MoS_2 flakes, despite their few-atom thicknesses. This structural sensitivity is a consequence of optical interference phenomena, which are acutely sensitive to changes in the optical path length, even down to the thickness of a MoS_2 monolayer. Accordingly, PEEM imaging based on deep-UV photoexcitation provides high sub-surface sensitivity. Functionally, the maps of resonance peak wavelength and total peak area shown in Fig. 3 are analogous to optical phase contrast images obtained with optical microscopy (i.e., Nomarski microscopy).[1,3] However, in the present study, the electron optics of PEEM renders intrinsically high spatial resolution.[16] Quantitative evaluation based on finite element analysis of the optical interference that results from the presence of MoS_2 flakes is a subject of future study.

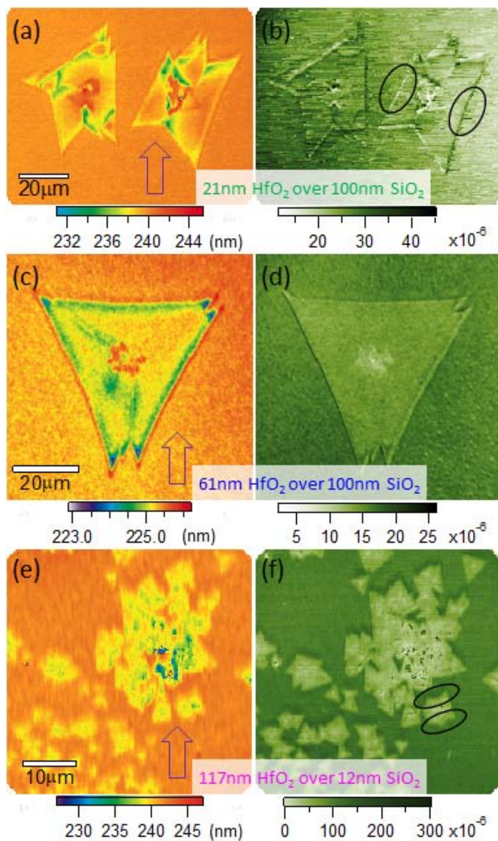

FIG. 3 Spatial mapping of cavity mode resonance peak wavelengths [(a), (c), and (e)] and total peak areas [(b), (d), and (f)] for samples with 21 nm- and 61 nm-thick HfO_2 overlayers on 100 nm-thick SiO_2, and 117 nm-thick HfO_2 overlayers on nominally 12 nm-thick SiO_2. The unit of total peak area is proportional to the wavelength times the photoemission yield. The arrows in (a), (c),

and (e) indicate the in-plane direction of the incident wavevector of deep-UV sample illumination. The ovals highlight the areas with contrast asymmetries (see the main text for details).

D. Extensions of PEEM-based sub-surface imaging

We tested the general applicability of this deep-UV PEEM approach to image atomically-thin MoS_2 flakes encapsulated by two other dielectrics commonly used in micro- and nanoelectronics. In Figs. 4 (a) and (b), we show sub-surface images of MoS_2 flakes sandwiched between the SiO_2 underlayer and overlayers of Al_2O_3 and SiO_2, respectively. In each case, MoS_2 flakes were clearly imaged, showcasing the extended applicability of this approach to other insulating or wide-band-gap materials.

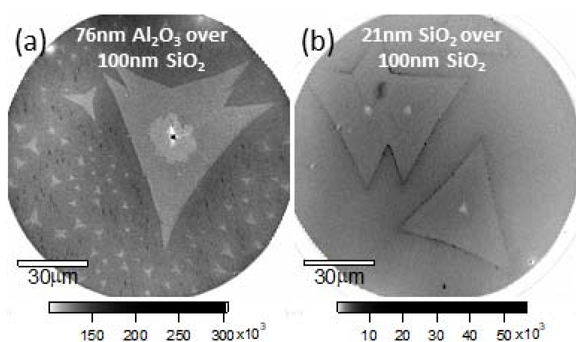

Fig. 4 PEEM images of MoS_2 flakes covered with various dielectric materials. (a) MoS_2 flakes sandwiched between 100 nm-thick SiO_2 (underlayer) and 76 nm-thick Al_2O_3 (overlayer). The CW light source is used for this measurement. See Photoemission electron microscopy measurement section of Supplemental Material[35] for detail. (b) MoS_2 flakes sandwiched between a 100 nm-thick SiO_2 (underlayer) and a 21 nm-thick SiO_2 (overlayer). We used the deep-UV laser light source for this measurement. The photon energy used for measurements in (a) and (b) was 5.9 eV (λ = 210 nm).

Finally, we note that the concept of sub-surface microscopy using deep-UV PEEM can be further extended by incorporating table-top, coherent and incoherent light sources. Controlling the polarization of light may offer additional insight for probing buried structures and their optical properties (i.e., functional imaging[2]). Such polarization-dependent measurement as well as optical standing wave measurement would be particularly useful when exploiting multi-photon photoemission processes[50] based on visible photoexcitation, where optical properties extracted for visible wavelengths would have broader scientific and technological impacts. We also expect that changing the energy or the incident angle of the light may enable tuning the sampling depth on-the-fly by shifting the region subjected to the high electromagnetic field. [20,22,51] Some of these imaging approaches are readily available for PEEM in a standard laboratory environment as various deep-UV light sources are emerging rapidly, with some becoming commercially-available in recent years.[52]

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[38] Fig. S2 shows a sequence of image contrast changes as a function of photoexcitation wavelength for the 103 nm-thick HfO_2 film on 100 nm-thick SiO_2, as well as 57 nm-thick HfO_2 and 117 nm-thick HfO_2 overlayers on nominally 12 nm-thick SiO_2. Similar image contrast appears for 61 nm-thick HfO_2 on a 100 nm-thick SiO_2 underlayer, not shown here, but quantified in Fig. 3.

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