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Abstract:

Hybrid heterostructures based on bulk GaN and two-dimensional (2D) materials offer novel paths toward nanoelectronic devices with engineered features. Here, we study the electronic properties of a mixed-dimensional heterostructure composed of intrinsic n-doped MoS₂ flakes transferred on p-doped GaN(0001) layers. Based on angle-resolved photoemission spectroscopy (ARPES) and high resolution X-ray photoemission spectroscopy (HR-XPS), we investigate the electronic structure modification induced by the interlayer interactions in MoS₂/GaN heterostructure. In particular, a shift of the valence band with respect to the Fermi level for MoS₂/GaN heterostructure is observed; which is the signature of a charge transfer from the 2D monolayer MoS₂ to GaN. ARPES and HR-XPS revealed an interface dipole associated with local charge transfer from the GaN layer to the MoS₂ monolayer. Valence and conduction band offsets between MoS₂ and GaN are determined to be 0.77 and -0.51 eV, respectively. Based on the measured work functions and band bendings, we establish the formation of an interface dipole between GaN and MoS₂ of 0.2 eV.

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I. INTRODUCTION

Among the vast collection of two-dimensional (2D) materials, transition metal dichalcogenides (TMDs) have attracted considerable interest for their unique layer-dependent electronic and optical properties[1,2]. TMDs such as MoS_2, $MoSe_2$, WS_2 and WSe_2 have tunable bandgaps from indirect in their bulk form to direct in the monolayer limit, then opening up their wide range of potential applications in nano- (opto-) electronics. For example, MoS_2, one of the most studied TMDs, has been used in field effect transistors[3] with excellent on/off ratio and room temperature mobility and in photodetectors[4] with high responsivity and fast photoresponse. On the other hand, the p-n junction is an elementary block of optoelectronics and its demonstration using 2D TMDs is a mandatory step toward the integration of these materials in real devices[5-10]. Interestingly, the combination of 2D materials grown on conventional 3D semiconductor is gaining importance for the design of electronic devices, since it combines the advantages of both the established 3D semiconductors and the unique properties of 2D materials. An interesting combination can be obtained using bulk semiconducting GaN and 2D materials[11-16] in the so called mixed-dimensional heterostructures[17], due to the maturity of planar GaN technology with a broad range of devices spanning from light emitting diodes to high power electronics[18]. Hence, hybridation of GaN with 2D TMDs such as MoS_2 is of particular relevance to design novel hybrid heterostructures. Since theoretical studies on such heterostructures are particularly challenging, experimental research works are mandatory to uncover the 2D TMD/3D heterostructure interfacial and electronic properties and trigger further theoretical efforts. This paper is dedicated to get deeper insight on the electronic properties of MoS_2/GaN heterostructure as well as interlayer interaction (*i.e.* charge transfer) between the two building blocks.

The GaN substrate is suitable for opto-electronic applications. The use of 2D materials and GaN demonstrates examples of a 2D/3D combination matching the general requirements for the vertical heterojunction bipolar transistor. When considering the devices architecture, the interaction between the 2D layered film and the substrate is crucial. Similarly to 2D van der Waals (vdW) heterostructures[19,20], two key issues have to be considered : the strain effect caused by the lattice mismatch between both materials constituting the heterostructures, and the band offsets resulting from the junction formation. Only two works by Tangi *et. al.* focused on the interface between GaN/MoS_2[15] and GaN/WSe_2[14]. The authors have grown undoped GaN on 2D materials and performed micro-Raman and X-ray photoemission spectroscopy (XPS) to investigate the properties of band alignment in these heterostructures. However for the optoelectronic applications, a n- or p-doped GaN is required. Ruzmetov D. *et al.*[11] have grown MoS_2 on n-type GaN/sapphire. Using conductive AFM (CAFM) they showed that the MoS_2/GaN heterostructure electrically conduct in the out-of-plane direction and across the van der Waals gap, forming a promising platform for vertical 2D/3D semiconducting devices. Moreover, Lee II E.W. *et al.*[13] realized a p-MoS_2/n-GaN heterojunction diodes. No Fermi level pinning was present at the interface and current-voltage measurement of the diodes exhibited excellent rectification. Besides, the influence of the stacking order can modify the electronic properties at the interface. In the meantime, to our knowledge, no work in the literature was performed using ARPES to study the electronic structure such as charge transfer, interface dipole and band bending at n-doped MoS_2 on p-doped GaN interface.

Based on these considerations, the impact of p-doped GaN as a substrate should not be overlooked. The investigation of electronic properties of MoS_2 combined with GaN becomes of fundamental importance. Therefore, based on Raman spectroscopy, we assess the strain sustained by the MoS_2 flakes, upon transfer on top of GaN. Next, by using angle resolved photoemission spectroscopy (ARPES), we show a significant charge transfer between MoS_2 monolayer and GaN(0001) layer. ARPES measurements showed that the GaN valence band maximum (VBM) shifts of about 300 meV towards the Fermi level compared to the VBM of pristine GaN(0001); implying electron transfer from the GaN layer to MoS_2. Thus, we expect that this experimental study, which offers a better understanding of these heterostructures, will provide sound guidelines towards real industrial applications and complement the recently introduced 2D/2D approaches[21,22] for which device growth and processing remain quite challenging to scale up.

II.   METHODS:

The 250 nm thick p-doped GaN was grown by plasma-assisted molecular beam epitaxy (MBE) on a SiC(0001) substrate. The growth was performed at 730 °C under Ga-rich conditions to favour the 2D growth following the Frank Van der Merve growth method. During the growth, the Mg cell was kept at 375 °C in order to induce a p-type doping of GaN layer[23]. Large scale MoS_2 monolayer flakes ($\approx$20 to $\approx$100 μm) have been grown by Chemical Vapor Deposition (CVD) on oxidized silicon substrate (see methods and ref[24]). The MoS_2 flakes transferred onto the GaN retain their triangular shapes with unchanged lateral sizes. Before any measurement, the MoS_2 sample was annealed at 300 °C for 30 min in ultra-high vacuum (P $\approx$ 10^{-10} mbar), in order to remove the residual surface contaminations induced by the wet transfer. The Raman and PL measurements were conducted using a commercial confocal Renishaw micro-Raman microscope with a 532 nm laser in ambient conditions of pressure and temperature. The excitation laser (wavelength 532 nm) was focused onto the samples with a spot diameter of ~1 μm and incident power of ~3 mW. The integration time was optimized in order to obtain an acceptable signal-to-noise ratio. PL measurements were performed on the same microscope with a 100× objective and a Si detector (detection range up to ~ 2.2 eV). XPS experiments were carried out on the TEMPO beamline (SOLEIL French synchrotron facility) at room temperature using a photon energy of 340 eV. The photon source was a HU80 Apple II undulator set to deliver linearly polarized light. The photon energy was selected using a high-resolution plane grating monochromator, with a resolving power E/ΔE that can reach 15,000 on the whole energy range (45 - 1500 eV). During the XPS measurements, the photoelectrons were detected at 0° from the sample surface normal n $\vec{}$ and at 46° from the polarization vector E $\vec{}$. The spot size was about 100 × 80 (H×V) μm². A Shirley background was subtracted in all core level spectra. The Mo 3d spectra were fitted by sums of Voigt curves, i.e, the convolution of a Gaussian (of full-width at half-maximum GW) by a Lorentzian (of full-width at half-maximum LW). The LW was fixed at 90 meV. The Ga 3d was fitted with a Voigt curve. The ARPES measurements were conducted at the CASSIOPEE beamline of Synchrotron SOLEIL. We used horizontal linearly polarized photons of 50 eV and a hemispherical electron analyzer with vertical slits to allow band mapping. The total angle and energy resolutions were 0.25° and 25 meV. The mean diameter of the incident photon beam was smaller than 50 μm. All ARPES experiments were done at room temperature. The Fermi level reference was taken at the leading edge of a clean metal (i.e. molybdenum clamps)

surface in electrical contact with the sample. The CL measurements were performed with an Attolight Chronos cathodoluminescence microscope operating at room temperature with 2 kV acceleration voltages. An IHR320 spectrometer (Jobin Yvon) coupled to a Newton CCD 920 camera (Andor/Oxford Instrument) was used to acquire the CL spectra. The final hypermap is a square matrix of 64x64 pixels, spanning about 30 microns wide, each of them containing a CL spectrum acquired in 1s. The simulations used to evaluate the CL excitation volume at 2 kV were performed using the CASINO v2.48 software (2D version), using a density of 6.15 g cm^{-3} for the GaN material.

III. RESULTS AND DISCUSSIONS

A 250 nm thick Mg-doped GaN(0001) (p-doped) grown by plasma-assisted molecular beam epitaxy (MBE) on SiC(0001) was used as a substrate. A few hundred micrometer wide monolayer MoS_2 flakes, grown by chemical vapor deposition (CVD) on SiO_2 substrate were transferred on the GaN layer by PMMA assisted technique[19] to build a MoS_2/GaN heterostructure as shown in Figure 1(a). An annealing process at T= 300 °C for 30 min was then used to clean the surface and the interface of our 2D/3D heterostructure. Owing to the large optical absorption of monolayer MoS_2, it is rather simple to identify MoS_2 flakes on the GaN surface as shown in the optical image in Figure 1(b). Hence, we can verify that the geometry and the sizes of the MoS_2 flakes are preserved during both transfer and annealing processes.

In Figure 1(c), we show the micro-Raman spectra, in the wavenumber range between 360 and 440 cm^{-1}, obtained for the MoS_2 transferred on GaN (black line)[1]. We can identify the two one-phonon Raman-active modes of monolayer MoS_2, namely the in-plane (E') and out-of-plane (A'$_1$) modes.[25,26] The frequency difference between the frequencies of the A'$_1$ and E' mode-features is ≈19-20 cm^{-1}, a value that is typical from pristine monolayer MoS_2 (see Fig. 1d).[19,27] The Raman intensity maps of the E' and A'$_1$ modes and the corresponding Raman frequency maps are shown in the supporting information Figure S1. The uniform intensity of both Raman modes illustrates the high quality and the absence of defects in our MoS_2 monolayers. The E' and A'$_1$ mode-frequencies display only minute spatial inhomogeneity of ≈ ± 1 cm^{-1} over a given MoS_2 single-domain (see Figure 1(d)). These results indicate that inhomogeneous strain due to the MoS_2 transfer process can be neglected. Figure 1(e) shows the photoluminescence (PL) spectrum for MoS_2/GaN measured at room temperature. On the PL spectrum, we identify the well-known A and B excitons located near 1.84 and 2 eV, respectively.[28] The A exciton energy is assigned to the optical band gap of MoS_2 on GaN, which is similar to the value found for van der Waals heterostructures such as MoS_2/graphene.[29] X-ray photoemission spectroscopy (XPS) and ARPES measurements were carried out for pristine GaN and MoS_2/GaN(0001) sample not only to investigate the atomic composition and the chemical bonding environment of the interface of our samples, but also to uncover the interface-based electronic properties of this heterojunction (band bending, work function, and dipole).

Figure 2(a) shows the XPS spectra of Ga-3d for MoS_2/GaN(0001) and the pristine GaN. In the two cases, only one peak is present corresponding to the Ga-N bonds. No oxidation was observed since the Ga-3d spectrum did not show any corresponding peak (expected at 1-1.2 eV higher binding energy (BE) with respect to the Ga-N peak[30,31]). After

the MoS_2 transfer on GaN, the Ga-3d peak shifts towards lower binding energy (about 200 meV). This shift at lower BE indicates a variation of the band bending, result of a charge redistribution at the MoS_2/GaN interface. This effect will be duly discussed in next sections.

The Mo-3d spectrum (in Figure 2(b)) contains one main doublet component at binding energy (BE) Mo $3d_{5/2}$ = 229.7 eV ($3d_{5/2}$:$3d_{3/2}$ ratio of 0.66 and a spin-orbit splitting of 3.10 eV[32]) related to a Mo^{4+} in a sulphur environment[33]. At lower BE (~ -0.52 eV) with respect to this main doublet peaks a small component is present (highlighted in green) which is the signature of a defective/sub-stoichiometric MoS_2 with sulfur vacancies (Sv)[33,34]. The weight of this component (between 10-15% of the whole Mo 3d spectrum) is not representative of a single MoS_2 flake due to the large X-ray spot size (~100 × 80 (H×V) μm^2), but it gives information on the percentage of defective MoS_2 in the explored area. The shoulder at BE = 226.5 eV represents the sulphur 2s peak. These BE values for the Mo 3d indicate an intrinsic n-type doping of the MoS_2 flakes[35]. No other components are present on the Mo 3d spectrum related to nitrogen, oxygen or carbon bonds[36–38] indicating that no contaminations are present on the sample and confirming the high quality of the interface of this hybrid heterostructure. Moreover, there is no signature of any chemical state associated with Mo or S in the Ga 3d core level spectrum which is a clear evidence of a van der Waals interaction between MoS_2 and GaN. This makes the heterointerface atomically abrupt without any inter-diffusion.

In order to investigate the band alignment and the electronic properties of the hybrid MoS_2/GaN heterostructure, we performed band structure measurements by angle-resolved photoemission spectroscopy (ARPES) at Cassiopée beamline of Synchrotron Soleil. The photoelectron intensity as a function of energy and k-momentum of pristine GaN(0001) and hybrid MoS_2/GaN(0001) are presented in Figure 3(a) and (b) respectively. The respective second-derivative spectra are provided in Figure 3(c) and (d) to improve the visibility of the band structure. The valence band structure of GaN is shown in Figure 3(a) and (c). From Figure 3(b) and (d), we notice the appearance of a new top-most band at around -1.5 eV, which is the signature of MoS_2 valence band. This confirms the high quality of the transferred MoS_2 within the hybrid heterostructure. We also can notice that the topmost band of GaN is upshifted upon the MoS_2 transfer.

In Figure 4 (a) is shown a vertical section at $k_{//}$= 0 Å^{-1} of the band structure of the MoS_2/GaN heterostructure and the pristine GaN. From the intersection of the linear extrapolation of the leading edge of the valence band spectrum with the baseline, we can locate the position of the valence band maximum (VBM) for the GaN in the heterostructure with respect to the pristine one. The relative VBM positions moved from 2.59 to 2.27 ± 0.05 eV for the GaN(0001) layer and the MoS_2/GaN heterostructure, respectively. This value is in agreement with the observed bandshift in ARPES measurements. This implies that valence band maximum (VBM) is getting closer to the Fermi level (located at 0 eV), reducing the band bending (V_{BB}) at the interface of about ΔV_{BB} = 0.32 eV. The valence band for the pristine GaN, was also measured with a photon energy hv =1300 eV (Figure S2). Using this photon energy, a probing depth of about 10 nm is reached, which is reasonably larger than the depletion region at the GaN interface. Then using the same procedure used in Figure 4, the distance of the valence band to the Fermi level E_v = 0.7 ± 0.05 eV in the bulk (*i.e.* in a flat band condition) was obtained. Considering that at the surface the VBM = 2.27 eV, a downward band bending of about 1.57 eV is present at the GaN(0001) surface. This band bending corresponds to an accumulation of

positive charge at the GaN surface, compensated by an opposite negative charge inside the semiconductor (*i.e.* depletion layer). When the MoS_2/GaN heterostructure is formed, this band bending is reduced. This effect is the result of electron transfer (interface dipole formation) from GaN(0001) in favor of MoS_2. From Figure 4(a) we are also able to infer more precisely the VBM for the MoS_2, VBM = 1.5 ± 0.05 eV, which implies a valence band offset between MoS_2 and GaN (ΔE_v) of about 0.77 eV. To gain insight into the electronic properties of the MoS_2/GaN interface, the work function of the heterostructure was compared to the work function of the pristine GaN *via* the measurement of the secondary electron cut off (Figure 4(b)). We found out a work function of ϕ=5.23 ± 0.05 eV for pristine GaN and ϕ=5.35 ± 0.05 eV for the hybrid MoS_2/GaN heterostructure. Based on literature about probing quasiparticle band structure by STM/STS[22], the band gap of MoS_2 is about 2.15 eV. This MoS_2 electronic band gap is larger than its optical band gap determined previously by PL spectroscopy (~1.84 eV, see Figure 1(e)) considering the large exciton binding energy in atomically thin TMDs[39]. The Cathodo-luminescence (CL) experiments described in Figure S3 were performed to further probe the MoS_2/GaN interface. From Figure 4(c), we determine a value of 3.41 ± 0.01 eV for the GaN optical gap at room temperature, consistent with the reported value of wurtzite GaN[40]. Considering the exciton binding energy in GaN of about 0.02 eV[30] we deduce a GaN excitonic gap of about 3.43 eV± 0.01 eV. Thus, with the known values of the band gaps (MoS_2 and GaN) the conduction band discontinuity ΔE_C is calculated from: $\Delta E_C = \Delta E_V - (E_{MoS2} - E_{GaN})$ where E_{MoS2} and E_{GaN} are the bandgap energies of MoS_2 and GaN, respectively; we obtain ΔE_C = -0.51 eV with type II band alignment at n-MoS_2/p-GaN heterojunction. This conduction band offset is close to the recently reported value (0.56 eV) for intrinsic epitaxial GaN/MoS_2,[15] with an inverted band position with respect to our work (*i.e.* the GaN CBM is at higher binding energy with respect to the MoS_2 CBM). A different band alignment was obtained in the case of n-doped GaN/p-doped MoS_2 [13] where a conduction band offset of 0.23 eV was measured. These results suggest the possibility of tuning the relative band alignment in the 2D/3D heterostructure and then the potential barrier height at the junction by varying the doping of the MoS_2 and the GaN layers. Although electronic properties in 2D materials are generally governed by interactions at the K points of the BZ due to direct bandgap around this particular point, the presence of a direct bandgap centered at the Γ point in the GaN electronic structure, suggests that charge transfer is not trivial in this heterostructure. By combining all the photoemission studies an interface electronic structure diagram is derived (Figure 5). These findings are in agreement with what was observed for WS_2/p-doped GaN[41] where an efficient charge transfer at the 2D-3D heterointerface was observed. In particular, Kummel *et al.* have shown that for this 2D/3D heterostructure the efficiency of the charge transfer across the heterointerface is influenced by the momentum mismatch of the VBM in the two semiconductors. Specifically, they underlined that the charge transfer process is more efficient when the excitation in the k space is near the Γ point of the 2D semiconductor, where a transfer to the 3D substrate is possible without a momentum change. At variance with metal, the work function of a semiconductor is not an intrinsic property, simply because the position of the Fermi level in the gap at the surface depends on the doping of the substrate which determines the amount of band bending. Moreover, when we form the MoS_2/GaN heterostructure a surface dipole ($\Delta\phi_{Dip}$) could be formed at the interface. This effect is described by the measured variation of work function of the system ($\Delta\phi$ = 0.12 eV). We have to take into account that in the case of a semiconductor the variation of band bending at the surface (ΔV_{BB} = 0.32 eV) also contributes to the total work function change. The effect of

dipole $\Delta\phi_{Dip}$ is assumed to change the electron affinity χ (where the electron affinity is the energy difference between the vacuum level E_{VAC} and the conduction band at the surface $E_{CBM)}$. Thus the total work function change $\Delta\phi$ due to the heterostructure formation is:

$$\Delta\phi = \Delta\chi + \Delta V_{BB} = \Delta\phi_{Dip} + \Delta V_{BB}$$

From this formula and the measured $\Delta\phi$ and ΔV_{BB} we calculate a surface dipole of $\Delta\phi_{Dip} = 0.2$ eV. This interface dipole is a consequence of interface electron redistribution between single layer of MoS_2 and GaN(0001). This does not imply any chemical bonding between the GaN and the MoS_2. Such charge redistribution at the interface between GaN and MoS_2 is also in agreement with GaSe/graphene[8,42] and graphene/MoS_2[29] heterostructures previously reported. It is interesting to underline also, that the Ga 3d core level peak shift by a lesser amount compared to the VBM after the heterostructure formation, this is probably related to this difference in the interface properties, *e.g.* this dipole formation.

IV. CONCLUSIONS

In summary, the interaction of n-doped single layer MoS_2 on top of p-doped GaN layer was systematically studied via various characterization methods. An interfacial charge transfer was highlighted within the hybrid heterostructure using ARPES. Based on our measurements we propose a band diagram model to explain the charge doping effect deducing a conduction band discontinuity of about $\Delta E_C = 0.51$ eV in a type II alignment configuration. The experimental band alignment is determined by XPS/ARPES measurements comparing the effect of MoS_2 transfer on the electronic structure of GaN. Therefore, the heterointerface formation gives rise to an additional dipole change of 0.2 eV which could shift the band edges with respect to each other. The band alignment obtained in the present paper is essential information for building electronic and optoelectronic devices based on GaN/monolayer MoS_2 and to a larger extent, for understanding the electronic coupling in 2D/3D heterostructures.

Figures captions:

Figure 1: a) Schematic of our MoS_2/GaN heterostructure; b) Optical image of MoS_2 transferred on GaN; c) Raman spectrum of MoS_2/GaN; d) hyperspectral Raman map of the difference between the frequencies of the A'_1 and E' mode features. e) Photoluminescence spectrum of MoS_2/GaN.

Figure 2: High-resolution XPS spectra of monolayered MoS_2/GaN heterostructure measured at $h\nu$ =340 eV; a) Ga-3d for GaN and MoS_2/GaN, b) Mo-3d for MoS_2/GaN

Figure 3: ARPES measurements of a) GaN and b) MoS_2/GaN measured at $h\nu$ =50 eV around the Γ point of Brillouin zones; the inserts in a) and b) correspond to the Brillouin zones of GaN and MoS_2/GaN respectively. c) and d) are the second-derivative spectra of a) and b) respectively, giving better visibility of the bands.

Figure 4: a) Integrated valence band at at $k_{//}$= 0 Å^{-1} of MoS_2/GaN and GaN at $h\nu$ =50 eV, b) Secondary electron cut-off *vs* kinetic energy of pristine GaN and MoS_2/GaN; c) Cathodo-luminescence of GaN.

Figure 5: Schematic of band alignment diagram of MoS_2/GaN heterostructure obtained from XPS/ARPES and CL measurements. The band gap values of MoS_2 and GaN have been obtained considering their excitons binding energies[30,39]. The solid and dashed lines correspond respectively to the band bending after and before MoS_2 transfer highlighting a variation of the band bending in GaN after MoS_2 transfer.

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a) hν = 340 eV
Ga 3d

Intensity (Arb. Units)

MoS$_2$/GaN

GaN

Binding Energy (eV)

b) hν = 340 eV

Intensity (Arb. Units)

Mo 3d

S 2s

Binding Energy (eV)

p-GaN

n-MoS$_2$

0.2 eV

4.39 eV

E_{Vac}

E_{Cond}

$\Delta E_C = 0.51$

E_F

1.5 eV

2.27 eV

0.7 eV

E_{Val}

0.32 eV