

Evolution of Electronic Structures of Polar Phthalocyanine–Substrate Interfaces

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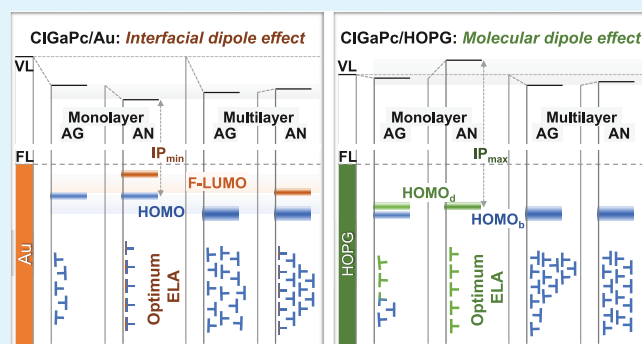
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ABSTRACT: The electronic structures and core-level spectra of chlorogallium phthalocyanine (ClGaPc) molecules of different thicknesses (submonolayer to multilayer) adsorbed on a polycrystalline Au substrate and a highly oriented pyrolytic graphite (HOPG) substrate, before and after thermal annealing, were investigated using photoelectron spectroscopic techniques for better understanding the charge-transfer properties. The energy-level diagrams (ELDs) of the ClGaPc thin films are found to evolve with film thickness, substrate nature, and thermal annealing. The interfacial dipole moment in the active Au substrate and the molecular dipole moment in the inactive HOPG substrate mainly dictate the ELD. Annealed monolayer films on both the substrates seem to adopt a similar well-ordered Cl-up orientated molecular organization, which is quite interesting, as it certainly indicates a substrate-nature-independent energy minimum configuration. The strong interaction of the active Au substrate gives rise to additional charge transfer and state transfer (of Ga) as evident from the formation of a former lowest unoccupied molecular orbital (F-LUMO) level in the highest occupied molecular orbital (HOMO) region and a low binding energy peak in the Ga $2p_{3/2}$ core level. The presence of strong F-LUMO and molecular-dipole-related HOMO_d levels in the predicted monolayer of well-ordered Cl-up oriented molecules on the Au and HOPG substrates, respectively, creates the optimum energy-level alignment (ELA) for both the systems, while the opposite shift of the vacuum levels in two different substrates makes the ionization potential (IP) for such a monolayer either minimum (on the Au substrate) or maximum (on the HOPG substrate), which is useful information for tuning the charge injection across the interface in organic semiconductor-based devices.

KEYWORDS: electronic structure, organic semiconductor, polar phthalocyanine, metal–organic interface, interfacial dipole, molecular dipole, charge transfer, photoelectron spectroscopy



1. INTRODUCTION

In the era of silicon, germanium, and other conventional inorganic semiconducting materials, organic semiconductors receive massive importance and research interest for different optoelectronic applications. The lack of control on material purity and structural ordering of the organic semiconductors compared to their inorganic counterparts, in the early days, was of real concern, but their easier and cheaper fabrication and large-scale applicability and versatility in the electronic industry subsided that concern to make them an important topic of research. Recently, organic light-emitting diodes (OLEDs)¹ have started to occupy the electronic market promoted by some excellent device manufacturing companies. On the other hand, organic photovoltaics (OPVs)² and organic thin-film transistors (OTFTs)³ are still lacking in the market, although extensive research works for the improvement of properties of these devices are underway all over the world.

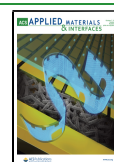
In most of the organic devices, an organic semiconductor is used as an active material and metals are used as electrodes;

hence, there are at least two metal–organic interfaces. Understanding such interfaces is of prime importance as the charge injection from a metal electrode to an organic active layer strongly depends on the charge injection barrier at the metal–organic interface.^{4,5} Several studies on different metal–organic systems have been carried out to investigate the electronic structure, in general, and the energy-level alignment (ELA),^{6–9} in particular, for the improvement of charge injection at the metal–organic interfaces. Phthalocyanine (Pc) is one such promising organic system that has high thermal and air stability. Pc and metallophthalocyanine (MPc), with extensive π -electron delocalization of the Pc rings, have

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attracted great attention of the scientists due to their unique physicochemical and electrochemical properties and possible applications in different fields including photodynamic therapy, catalysis, and nonlinear optics and as active materials in organic electronic devices.^{3,10–14} MPc can be either polar or nonpolar. Nonpolar MPc has a negligible dipole moment due to its symmetric planar structure, while polar MPc (shown in Figure 1) can have a finite dipole moment depending on its molecular orientation.⁸

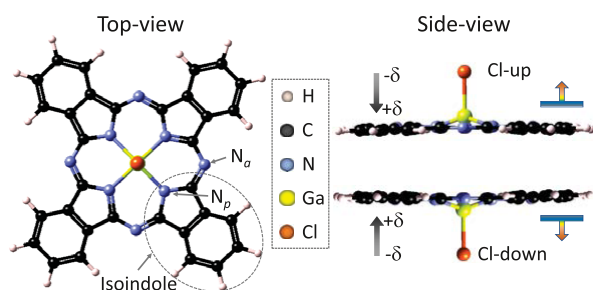


Figure 1. Structure of a polar chlorogallium phthalocyanine (ClGaPc) molecule. Top view or the Lewis structure of the molecule indicating four isoindole groups connected through four aza-bridging nitrogen (N_α). Pyrrole nitrogen (N_β) in each isoindole is also indicated. Side view of the molecule indicating possible Cl-up and Cl-down configurations. Schematics of such configurations and respective polarity of the dipole are also indicated.

The possibility of having preferred orientation and finite dipole moment of polar MPc (as shown schematically in Figure 1) encouraged many to study its molecular orientation-dependent electronic structure. For example, the role of structural imperfection in the electronic structures of chloroaluminum-phthalocyanine (ClAlPc) on a highly oriented pyrolytic graphite (HOPG) substrate has been studied using ultraviolet photoelectron spectroscopy (UPS) and metastable atom electron spectroscopy techniques, where serious band bending and changes in the ELA are observed.⁷ The molecular orientation-dependent electronic properties of ClAlPc on Au(111) have been investigated using UPS and scanning tunneling microscopy techniques, where a mixed (Cl-up and Cl-down) and fixed (Cl-up) oriented molecules are observed on the as-grown and the thermally annealed films.⁸ The coverage-dependent work function and spectral line shapes of occupied molecular energy states and the molecular orientation-dependent ELA of ClAlPc grown on the Ag(111) substrate have been studied using angle-resolved photoemission spectroscopy, which shows that the dipole orientation in the ClAlPc monolayer can be controlled by adjusting the deposition rate and postannealing conditions.⁹ The molecular orientation and growth mechanism of ClAlPc and chlorogallium phthalocyanine (ClGaPc) on a flat Au(100) single crystal and rough indium tin oxide-coated glass have also been studied using X-ray absorption spectroscopy and Raman spectroscopy for relatively thick films.¹⁵ Orientational ordering of ClGaPc on Cu(111) in the submonolayer coverage has been studied using the X-ray standing wave technique, which indicates that the ClGaPc molecules adsorb the highly reactive Cu substrate in a Cl-down configuration by forming a covalent bond.¹⁶ Despite a large number of studies on polar MPc,^{7–9,15,16} the proper understanding of the electronic structure and interaction of ClGaPc molecules on/with Au substrate, in general, and polycrystalline Au substrate, in particular (which

better resembles the electrode structure compared to the crystalline Au substrate), is still lacking.

In the present work, we have tried to address these issues by studying the electronic structures and the molecule–substrate interactions of the as-grown and thermally annealed ClGaPc/Au interfaces for different film thicknesses of ClGaPc molecules on (111) textured polycrystalline Au substrate, in comparison with the ClGaPc/HOPG interfaces, using in situ ultraviolet and X-ray photoelectron spectroscopy (UPS and XPS) techniques. In fact, splitting of the Ga $2p_{3/2}$ core-level peak into two, with a finite binding energy separation (around 1.1 eV) and variable peak intensities due to thermal annealing, was observed in ClGaPc/Au films, unlike the ClGaPc/HOPG films, for the first time. Also, the emergence of an intense band between the highest occupied molecular orbital (HOMO) level and the substrate Fermi level (FL), known as the former lowest unoccupied molecular orbital (F-LUMO) level,^{17,18} was observed after thermal annealing in the ClGaPc/Au films, unlike the ClGaPc/HOPG films. Such observations, which seem to indicate a strong molecule–substrate interaction at the metal–organic interface and the subsequent thermal-annealing-promoted preferential orientation (namely, Cl-up configuration) of the molecules at that strongly interacting ClGaPc/Au interface, are quite interesting and can be rationalized further in terms of chemical bonding, charge transfer, charge reorganization, and site specificity.

2. EXPERIMENTAL DETAILS

The UPS and XPS measurements of the substrates and the deposited ClGaPc films were carried out in an ultrahigh vacuum (UHV) multiprobe setup (Omicron Nanotechnology) at a base pressure of $\sim 2.0 \times 10^{-9}$ mbar, which was equipped with an EA125 hemispherical energy analyzer and two light sources.^{19–21} For the UPS measurements, a He gas discharge lamp of 21.2 eV photon energy was used as the source and the corresponding spectrometer energy resolution was ~ 0.1 eV. The UPS measurements were carried out by applying a sample bias of -6.0 V to determine the high binding energy cutoff (HBEC) with respect to the substrate FL of a spectrum. It can be noted that the difference between the incident photon energy and the HBEC defines the vacuum level (VL). UPS spectra were collected at a 90° take-off angle. A higher emission angle was chosen to maximize the photoelectron yield. For the XPS measurements, monochromatic Al $K\alpha$ X-ray of 1486.6 eV photon energy was used as a source and the corresponding spectrometer energy resolution was ~ 0.8 eV. Polycrystalline Au (coated on Si) and HOPG were selected as the substrates for the present study and Au $4f_{7/2}$ level (binding energy of 84.0 eV)¹⁹ and C 1s level (binding energy of 284.4 eV for HOPG)^{22,23} were chosen as the respective reference levels (shown in Figure S1 in the Supporting Information) to calibrate the other core-level spectra. Prior to insertion into the UHV chamber, Au substrates were annealed in vacuum to increase Au(111) texture, which was confirmed by X-ray diffraction (XRD) and rocking scan measurements carried out using the VXRd setup.^{24,25} Inside the UHV chamber, the Au substrates were cleaned by Ar^+ ion sputtering and examined by XPS. Prior to insertion into the UHV chamber, the top layer of the HOPG substrate was peeled off to get a clean HOPG surface.

A deposition chamber, attached with a characterization chamber, was used for film deposition. The ClGaPc molecules, purchased from Sigma-Aldrich (purity $\sim 97\%$), were deposited on clean Au and HOPG substrates by the thermal evaporation technique at an evaporation temperature of $288^\circ C$ and at a base pressure of $\sim 2.2 \times 10^{-8}$ mbar. The ClGaPc films of nominal thicknesses of 3, 5, and 15 Å, which represent about 0.9, 1.4, and 4.3 monolayer thicknesses (considering monolayer thickness of ≈ 3.5 Å, as reported before⁸), i.e., submonolayer, within monolayer and bilayer, and multilayer coverage, respectively, were deposited on the substrates at room temperature

and at a fixed deposition rate (1.2 Å/min) by varying the deposition time. The deposition rate was monitored with a previously calibrated quartz crystal microbalance (QCM). All of the films, immediately after deposition (i.e., as-grown or AG) and also after annealing at 150 °C for 4 h (i.e., annealed or AN) in UHV conditions, were characterized using UPS and XPS techniques at room temperature. The annealing condition was selected according to the well-established procedure for the preparation of an ordered film with negligible molecular desorption during annealing.⁷ The Shirley method was used to subtract the background, while the Gaussian–Lorentzian (GL) sum function was used to fit the XPS core-level spectra.

Topographical images of a thick film (both AG and AN) were collected using an atomic force microscope (CSI Nano-Observer)²⁶ in the tapping mode with a gold-coated Si tip (radius of curvature, ~10 nm; resonant frequency, ~60 kHz). Atomic force microscopy (AFM) images were processed using free Gwyddion software.²⁷

3. RESULTS AND DISCUSSION

3.1. Interfacial Interaction. The effect of interfacial interaction on the vacuum and HOMO levels of the ClGaPc/Au and ClGaPc/HOPG systems, which were investigated by studying the evolution of the UPS spectra near the HBEC and FL or HOMO regions, are presented and discussed here.

3.1.1. UPS Study of the ClGaPc/Au System. The UPS spectra of the ClGaPc/Au thin films of different thicknesses are shown in Figure 2 ((a, b) for the AG films, while (c, d) for the

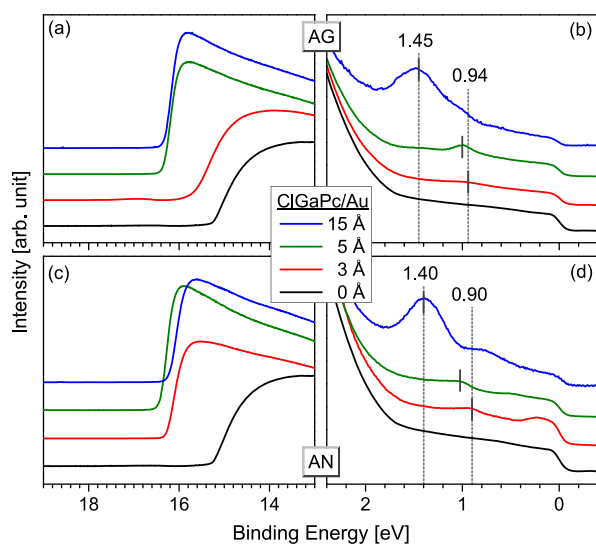


Figure 2. UPS spectra of the ClGaPc/Au thin films of different thicknesses (0, 3, 5, and 15 Å). (a, b) UPS spectra of the as-grown (AG) films. (c, d) UPS spectra of the thermally annealed (AN) films. (a, c) HBEC region of the spectra. (b, d) HOMO region of the spectra.

AN films). The HBEC regions of the spectra of the AG and AN films are shown in Figure 2a,c, respectively, which provide the VL corresponding to each spectrum (see Figure S2 and Table S1 of the Supporting Information for the detailed estimation). The shift of VL due to molecular adsorption and subsequent thermal annealing, with respect to the substrate VL, is an important parameter, which is used here for further discussion. A small VL shift of about -0.4 eV is observed in the AG 3 Å film, which becomes quite appreciable (about -1.0 eV) after annealing. In the 5 Å film, an appreciable VL shift of about -1.0 eV in the AG condition and an almost similar shift

(about -1.1 eV) after annealing are observed. Finally, in the AG 15 Å film, a similar VL shift of about -1.0 eV is observed, which becomes about -0.9 eV after annealing.

The small VL shift in the AG 3 Å (i.e., submonolayer thick) film can be attributed to the push-back effect, which is a manifestation of a weak molecule–substrate interaction.^{6,8,19} A less ordered island-type growth of the ClGaPc molecules having a mixed (Cl-up and Cl-down) configuration is likely, as the island-type growth can provide small coverage and the mixed configuration can provide a weak molecule–substrate interaction, hence a small VL shift in combination. The increased VL shift after annealing probably suggests an increase in the monolayer coverage and the molecule–substrate interaction leading to the ordering of the molecules in the preferred configuration, presumably the Cl-up configuration, similar to that reported previously for the ClAlPc/Au(111) system.^{7,8} The large VL shift in the AG 5 Å (i.e., above monolayer thick) film can be attributed to the increase in the push-back effect due to the increase in the coverage of the film. Almost no change in the VL shift after annealing indicates the saturation of that push-back effect probably due to the full or maximum coverage of the AG film, where even further ordering of the molecules after annealing can not create any appreciable effect on the VL. A similar large VL shift in the AG 15 Å (i.e., multilayer thick) film suggests that the saturated push-back is the only dominant effect after full coverage. The slight decrease in the VL shift of this film after annealing indicates some weakening in the molecule–substrate interaction, probably due to a change in the dipole moment or molecular orientation along with a charge reorganization at the interface in presence of the molecules above monolayer.

The HOMO region of the UPS spectra of the AG and AN ClGaPc/Au thin films are shown in Figure 2b,d, respectively. A thickness-dependent shift of the HOMO peak (marked in the figure) is observed. The position of the HOMO peak for the 3 Å film is found near 0.9 eV, which shifted to near 1.0 and 1.4 eV for the 5 and 15 Å films, respectively. This thickness-dependent shift of the HOMO level in the ClGaPc/Au system can be correlated with the typical band bending phenomena caused by local work function.^{6,18,19} Generally, there is a difference between the FLs of the metal substrate and the adsorbed molecular layer, which creates an electronic in-equilibrium at the interface. This in-equilibrium leads to charge redistribution at the metal–organic interface and consequently a thickness-dependent shift of the HOMO levels towards the higher binding energy side.⁶ Other important phenomena, like interfacial dipoles and push-back effects, also strongly influence the charge redistribution at the interface, which are likely to affect the HOMO level and cause a serious band bending. No appreciable change of the HOMO level after thermal annealing is observed for the ClGaPc/Au films. However, a new peak, in addition to the HOMO peak, is observed (Figure 2d) for all of the AN films. This new peak basically represents a F-LUMO level as observed previously in some planner phthalocyanines^{18,28–30} and other organic materials^{31,32} of monolayer and submonolayer coverage.

The presence of a partially filled F-LUMO level is the indication of a strong interaction between the interfacial molecules and the metallic substrate through charge transfer from the substrate to the interfacial molecular layer or through some chemical interaction at the interface.^{18,28–32} Interestingly, such interaction seems to depend on the specificity of

the central metal (M) atoms of MPC molecules and the metal substrate. The presence of F-LUMO peaks in the present case indicates a strong interaction between ClGaPc molecules and the Au substrate through the Ga site as also evident from the Ga $2p_{3/2}$ core-level spectra later, while the absence of a F-LUMO peak in the case of the CuPc/Au film indicates a lack of a strong interaction between CuPc molecules and the Au substrate.³⁰ It is also evident that the formation of a F-LUMO peak suppresses the clear double-peak nature of HOMO, rather making it an asymmetric peak, which is apparent here and also for the monolayer thick SnPc/Ag film and 4 Å thick CuPc/Ag film.^{28,30} This is probably due to the strong interaction (or charge transfer)-induced transfer of occupied levels from HOMO to F-LUMO. On the other hand, the absence of a F-LUMO peak helps to observe the clear double-peak nature of HOMO as evident in the thick SnPc/Ag film and also in the 4 Å thick CuPc/Au film.^{28,30}

A F-LUMO peak at a binding energy of 0.2 eV is observed in the AN 3 Å film, the intensity of which is equal to that of the HOMO peak, as clearly shown in Figure 3a. This indicates that

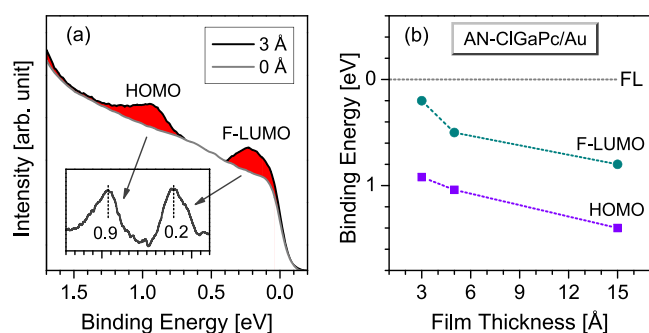


Figure 3. (a) Magnified view of the HOMO region of the 3 Å AN ClGaPc/Au film, showing positions and intensities (relative to the substrate) of the HOMO and F-LUMO levels. (b) Variation of HOMO and F-LUMO levels with the thickness for the AN ClGaPc/Au films. The position of the reference FL is indicated.

the molecules in the AG condition adsorb or interact weakly with the substrate (physisorption) but after annealing interact strongly with the substrate through charge transfer from the substrate to molecules or forming some chemical bonds (chemisorption), which is also consistent with the result of the VL shift. The F-LUMO, which is at 0.2 eV in the 3 Å film, is found at 0.5 and 0.8 eV in the 5 and 15 Å films, respectively. The variations of the F-LUMO and the HOMO levels with the film thickness for the AN ClGaPc/Au films are shown in Figure 3b. A gradual shift of the F-LUMO level toward the higher binding energy with increasing film thickness, similar to that of the HOMO level, can be attributed to the band bending of the molecular orbitals of the ClGaPc/Au films, as discussed earlier. A decrease in the intensity of the F-LUMO level, with respect to that of the HOMO level, from 1.0 (for the 3 Å film) to 0.1 (for the 15 Å film) with increasing film thickness is observed, probably due to the prominent molecule–substrate interaction only up to the monolayer coverage.

3.1.2. UPS Study of the ClGaPc/HOPG System. The UPS spectra of the ClGaPc/HOPG thin films of different thicknesses are shown in Figure 4 ((a, b) for the AG films, while (c, d) for the AN films). The HBEC regions of the spectra of the AG and AN films are shown in Figure 4a,c, respectively, which provide the VL corresponding to each

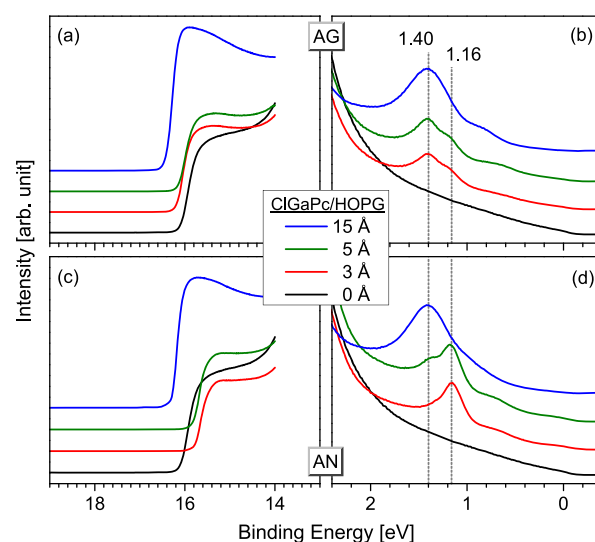


Figure 4. UPS spectra of the ClGaPc/HOPG thin films of different thicknesses (0, 3, 5, and 15 Å). (a, b) UPS spectra of the as-grown (AG) films. (c, d) UPS spectra of the thermally annealed (AN) films. (a, c) HBEC region of the spectra. (b, d) HOMO region of the spectra.

spectrum (see Figure S3 and Table S2 of the Supporting Information for the detailed estimation). A negligible (about -0.1 eV) VL shift with respect to the substrate is observed in the AG 3 Å film, which becomes about $+0.3$ eV after annealing. A similar nature is observed for the 5 Å film, while for the 15 Å film, a shift of about -0.3 eV for the AG film becomes about -0.2 eV after annealing. This observation for the ClGaPc/HOPG system is completely different from that for the ClGaPc/Au system.

The negligible VL shift in the AG 3 Å film can be considered as a net result of two opposite effects: a negative and a positive shift, presumably from the bilayer and single molecular layer structures on the HOPG substrate (even for the submonolayer ClGaPc coverage), respectively. The formation of a highly ordered single molecular layer structure with a net molecular dipole moment due to a definite molecular orientation (presumably Cl-up) after annealing is likely to affect the VL and provide a positive shift, as reported previously for ClGaPc/HOPG⁹ and also for some other polar phthalocyanines on HOPG.^{8,33} On the contrary, the bilayer structure, having a mixed (Cl-up and Cl-down) molecular configuration and negligible molecular dipole moment, is likely to provide a negative shift. In the case of the AG 5 Å film, it is basically the same combination of the structure. After annealing, an increase of the ordered single molecular layer structure provides a positive VL shift. In the 15 Å film, a negative VL shift basically reflects the simple coverage of the substrate with molecules, presumably a stacked bilayer structure (order or disorder) with negligible molecular dipole moment, whereas a very small positive change after annealing suggests a slight development of molecular dipole moment near the film–substrate interface, presumably due to a small change in the structure of the film through molecular reorganization.

The HOMO regions of the UPS spectra of the AG and AN ClGaPc/HOPG thin films are shown in Figure 4b,d, respectively, where a thickness-dependent HOMO band structure is observed. In fact, each HOMO band can be considered as a convolution of two peaks, whose positions are

fixed (at around 1.2 and 1.4 eV) but intensities are different. In the AG 3 Å film, both peaks of nearly equal intensity are observed, which after annealing almost convert into a single peak at around 1.2 eV. In the AG 5 Å film, both peaks of nearly equal intensity but intense compared to those of the AG 3 Å film are observed. After annealing, the intensity of the peak at around 1.2 eV increases, while that of the peak at around 1.4 eV decreases. In the 15 Å film, only a broad single peak at around 1.4 eV is observed.

The origin of the two distinct peaks at the HOMO level is likely to be related to the different molecular orientations. The peak at the lower binding energy side can be assigned to a layer of molecules in the Cl-up configuration, while the peak at the higher binding energy side can be assigned to a layer of molecules in the Cl-down configuration or a bilayer stack of molecules in Cl-up and Cl-down combination, as reported before.^{8,9,34} In the 3 Å film, the presence of two distinct peaks can be correlated to these two layers of different molecular configurations. After annealing, the conversion to a single peak at the lower binding energy position indicates the ordering of the molecules, predominantly with the Cl-up configuration.^{8,9} In the AG 5 Å film, two peaks of almost equal intensity also appear from two layers of different molecular configurations. After annealing, improved ordering likely to place a large number of molecules (almost full coverage) with the Cl-up configuration in the first layer and the remaining limited number of molecules with the Cl-down configuration in the second layer to form an intense lower binding energy peak and a weak higher binding energy peak. A broad single peak at the higher binding energy position in the 15 Å film can be correlated to the disordered bilayer stacks, the structure of which almost remains unchanged after annealing. The absence of a noticeable lower binding energy peak, even after annealing, can be correlated to the lack of appreciably ordered Cl-up configuration molecules near the interface, probably due to the presence of a thick molecular overlayer.

3.2. Site-Specific Interaction. The site-specific information along with the molecule–substrate interaction and their effect on the local electronic structures of the ClGaPc/Au and ClGaPc/HOPG films, which were investigated by studying the evolution of the C 1s, N 1s, and Ga 2p_{3/2} core-level XPS spectra, is presented and discussed here.

3.2.1. XPS Study of the ClGaPc/Au System. The C 1s core-level spectra of the AG and AN ClGaPc/Au thin films of different thicknesses are shown in Figure 5. All spectra were fitted with four distinct peaks of similar width (full width at half-maximum (FWHM) \approx 1.1 eV), two main peaks arising from the benzene and pyrrole carbons (C_C and C_N) and two secondary peaks arising from their π - π^* shake-up satellites (S_C and S_N), as modeled previously.^{28,30,35,36} The S_C and S_N satellite peaks are mostly found at a distance of 1.9 ± 0.1 eV from the respective main peaks toward the higher binding energy side. The C_C and C_N peaks in the 3 Å film were found at 284.2 and 285.3 eV, those in the 5 Å film were found at 284.4 and 285.6 eV, and those in the 15 Å film were found at 284.6 and 285.9 eV, respectively, indicating a small gradual shift of the peaks with the film thickness. Such a small shift of peaks toward lower binding energies with decreasing thickness from a multilayer to a submonolayer can be correlated to the shift in the core levels due to band bending associated with charge reorganization or transfer at the interface arising from the molecule–substrate interaction.^{28,30,37} This is interesting as it suggests that the effect of band bending or charge

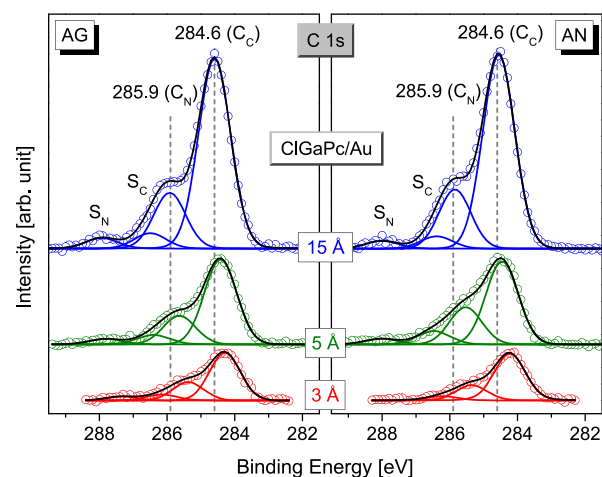


Figure 5. C 1s core-level spectra of the ClGaPc/Au thin films of different thicknesses (3, 5, and 15 Å) before (AG) and after (AN) thermal annealing, showing a thickness-dependent shift of the four deconvoluted peaks corresponding to the benzene and pyrrole carbons (C_C and C_N) and their shake-up satellites (S_C and S_N), and the final positions of the C_C and C_N peaks.

reorganization due to the interfacial dipoles not only affects the molecular levels (as observed in the HOMO region of the UPS spectra) but also the core levels. Also, the separation between the C_C and C_N peaks was found to change with the film thickness. A decrease in separation with decreasing thickness indicates that the shift of the C_N peak is more compared to that of the C_C peak when the film thickness decreases from a multilayer to a submonolayer. This result suggests that due to the molecule–substrate interaction, the ClGaPc molecules adjacent to the Au surface, get perturbed a bit and the effect is more on pyrrole carbons compared to that on benzene carbons.^{28,30} On the other hand, no appreciable change in the C 1s spectra of the films after AN indicates not much effect of thermal annealing on the C 1s core level.

The N 1s core-level spectra of the AG and AN ClGaPc/Au thin films of different thicknesses are shown in Figure 6. In a single ClGaPc molecule, there are eight N atoms; among them,

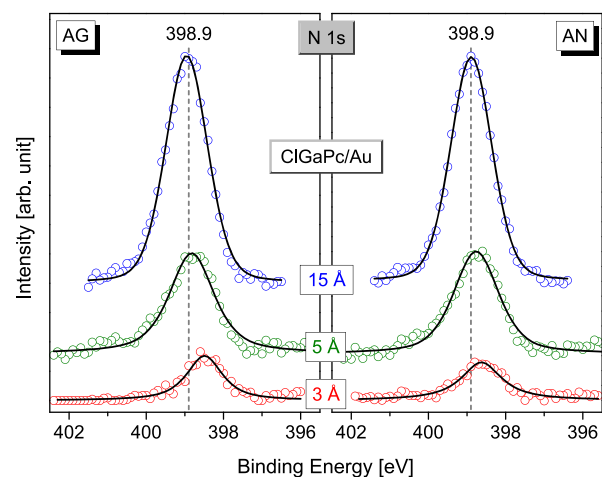


Figure 6. N 1s core-level spectra of the ClGaPc/Au thin films of different thicknesses (3, 5, and 15 Å) before (AG) and after (AN) thermal annealing, showing a thickness-dependent shift of the peak and the final peak position.

four are pyrrole nitrogen (N_p) and the other four are azaporphyrine or aza-bridging nitrogen (N_a), as shown in Figure 1. The chemical states of the N_p and N_a atoms are quite similar; hence, the binding energy difference between the core levels of these two different N atoms is very small (around 0.28 eV, according to the reported density functional theory (DFT) calculations).^{38,39} It is thus very difficult to resolve these two peaks. Accordingly, each N 1s spectrum was fitted with a single peak, as shown in Figure 6. The N 1s peak in the 3 Å film was observed at 398.5 eV, while those in the 5 and 15 Å films were found at 398.7 and 398.9 eV, respectively. The position of the N 1s peak in the 15 Å film is consistent with that reported in the literature for the thick ClGaPc film.⁴⁰ A satellite peak was also expected but could not be resolved here. Although there was a shift in the N 1s spectra with the thickness, almost no change in the spectra of the films was noted after annealing. The shift of the N 1s peak (about 0.4 eV) toward lower binding energy with decreasing thickness is similar to that of the C 1s spectra, which confirms or substantiates the molecule–substrate interaction and the interfacial charge reorganization or transfer phenomenon at the ClGaPc/Au interface, as mentioned before.

Next, the Ga $2p_{3/2}$ core-level spectra of the AG and AN ClGaPc/Au thin films of different thicknesses are shown in Figure 7. All spectra were fitted with two peaks, a low binding

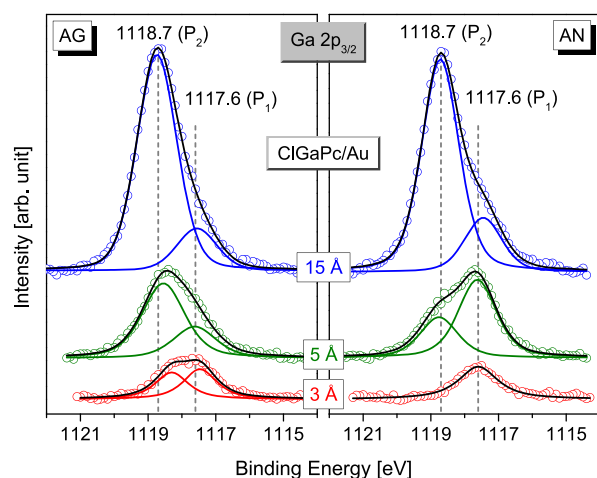


Figure 7. Ga $2p_{3/2}$ core-level spectra of the ClGaPc/Au thin films of different thicknesses (3, 5, and 15 Å) before (AG) and after (AN) thermal annealing, showing a thickness-dependent shift of the two deconvoluted peaks, P_1 and P_2 , corresponding to the substrate interacting and noninteracting Ga atoms, respectively, and their final positions.

energy peak (P_1) and a high binding energy peak (P_2). In the AG 3 Å film, the two peaks P_1 and P_2 are found at 1117.5 and 1118.3 eV, respectively. The intensity ratio (I_1/I_2) of the peaks P_1 and P_2 is ~ 1.1 . After annealing, the P_2 peak almost disappears and a strong peak P_1 at 1117.6 eV is only observed (i.e., $I_1/I_2 \rightarrow \infty$). In the AG 5 Å film, P_1 and P_2 peaks are observed at 1117.6 and 1118.6 eV, respectively, with $I_1/I_2 \approx 0.4$. After annealing, the P_1 and P_2 peaks are found at 1117.6 and 1118.8 eV, respectively. The intensity of the P_2 peak is found to decrease, while that of the P_1 peak is found to increase drastically, with a large change in the value of I_1/I_2 from ~ 0.4 to ~ 1.9 . Finally, in the 15 Å film, the P_1 and P_2 peaks are found at 1117.6 and 1118.7 eV, respectively, with

almost no change in the peak positions but a slight increase in the value of I_1/I_2 from ~ 0.2 to ~ 0.3 after annealing.

Thus, in general, each Ga $2p_{3/2}$ core-level spectrum can be considered as a convolution of two peaks, P_1 and P_2 , at 1117.6 ± 0.1 and 1118.7 ± 0.1 eV, respectively, with a separation of 1.1 ± 0.1 eV and a peak width (FWHM) of 1.3 ± 0.1 eV but of different I_1/I_2 values. The appearance of double peaks in the Ga $2p_{3/2}$ core-level spectra of the ClGaPc molecules is quite interesting, as such splitting has not been observed before. However, similar splitting has been observed in the Cu $2p_{3/2}$ spectra of CuPc molecules when deposited on the 7×7 reconstructed Si(111) surface.³⁵ The appearance of a low binding energy peak in the monolayer range films, in addition to its usual Cu(II) peak, was attributed to the partial reduction of the Cu(II) atoms to Cu $3d^{10}$ due to the strong interaction of the molecule with the Si(111) surface. Similarly, in the present case, the P_2 peak is due to the usual Ga atoms, namely, Ga(III), while the P_1 peak can be attributed to the partially reduced Ga atoms, which take place due to the strong interaction of the ClGaPc molecules with the Au surface. Such interaction is only possible with the near-substrate Ga atoms, i.e., with the ClGaPc molecules in the first layer having a Cl-up configuration. Hence, the molecules with the Cl-up configuration near the Au substrate only contribute to the P_1 peak, while the rest of the molecules contribute to the P_2 peak.

Accordingly, in the AG 3 Å (i.e., submonolayer range) film (for $I_1/I_2 \approx 1.1$), the ClGaPc molecules are in the first layer with both Cl-up and Cl-down configurations, while after annealing (for $I_1/I_2 \rightarrow \infty$), all of the molecules are in the first layer with the Cl-up configuration only. However, in the 5 Å (i.e., sub-bilayer range) film (for $I_1/I_2 \approx 0.4$), initially, the molecules are in the mixed configuration/orientation with a limited number of near-substrate molecules in the Cl-up configuration and after annealing (for $I_1/I_2 \approx 1.9$) majority of the molecules (which can be accommodated in a single layer) are in the first layer (nearly filled) with the Cl-up configuration and the remaining molecules are in the second layer preferably with the Cl-down configuration. Similarly, in the 15 Å (i.e., multilayered) film (for $I_1/I_2 \approx 0.2$), initially, the molecules are in the mixed configuration/orientation and after annealing (for $I_1/I_2 \approx 0.3$) most of the molecules in the first layer are in the Cl-up configuration. It can be noted that due to the presence of a thick molecular overlayer (which contributes to the P_2 peak), the change in the I_1/I_2 value or P_1 peak intensity after annealing (which is due to the change in the molecular configuration in the first layer) in the latter film is very small, as expected.

3.2.2. XPS Study of the ClGaPc/HOPG System. The C 1s spectra of the ClGaPc/HOPG films, although investigated, are not shown here, as the signals from the ClGaPc carbon atoms are suppressed by the substrate (HOPG) carbon atoms. The N 1s spectra of the AG and AN ClGaPc/HOPG thin films of different thicknesses are shown in Figure 8. The N 1s peak is found at 398.9 ± 0.1 eV for all of the AG and AN films, indicating no effect of film thickness or annealing on the N 1s core level of the film. The FWHM value of the peak is also found to be almost the same for all of the spectra except for the spectra of the AN 3 and 5 Å films, where a small decrease with respect to the AG films is observed, which indicates the ordering of the molecules after annealing, as suggested by the UPS results. The N 1s peak position in the ClGaPc/HOPG films is similar to that in the 15 Å (multilayered) ClGaPc/Au film, which is also the position in the thick ClGaPc film

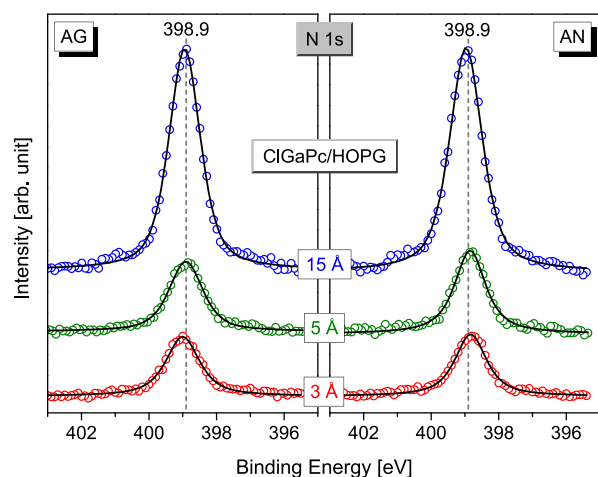


Figure 8. N 1s core-level spectra of the ClGaPc/HOPG thin films of different thicknesses (3, 5, and 15 Å) before (AG) and after (AN) thermal annealing, showing no thickness-dependent shift of the peak, unlike ClGaPc/Au thin films.

reported in the literature.⁴⁰ The lack of the film thickness effect on the N 1s core level indicates that the HOPG substrate does not interact with the ClGaPc molecules, unlike the Au substrate. This also means that the HOPG surface is (or behaves as) an inert surface for the ClGaPc molecules.

Finally, the Ga $2p_{3/2}$ core-level spectra of the AG and AN ClGaPc/HOPG thin films of different thicknesses are shown in Figure 9. Only a single peak at 1118.6 ± 0.1 eV is found in

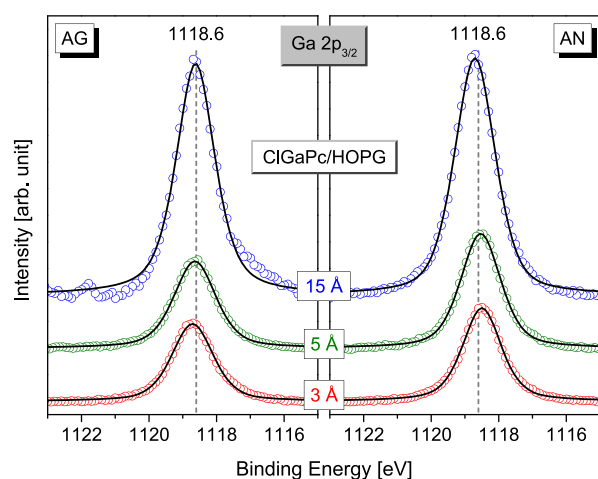


Figure 9. Ga $2p_{3/2}$ core-level spectra of the ClGaPc/HOPG thin films of different thicknesses (3, 5, and 15 Å), before (AG) and after (AN) thermal annealing, showing no splitting or thickness-dependent shift of the peak, unlike ClGaPc/Au thin films.

every Ga $2p_{3/2}$ spectra. The FWHM of the peak is found to be almost the same for all of the spectra except for the spectra of the AN 3 and 5 Å films, where a small decrease with respect to the AG ones is observed. This observation is consistent with that of the N 1s spectra and UPS spectra of the ClGaPc/HOPG films, as discussed before, suggesting further that the molecules in the 3 and 5 Å films became ordered after annealing. That is, after annealing, all molecules in the submonolayer film are ordered or arranged in the first layer with the Cl-up configuration, while those in the sub-bilayer film are arranged either in the monolayer with the Cl-up

configuration or bilayer with Cl-up and Cl-down configurations. The thickness-independent behavior of the Ga $2p_{3/2}$ spectra confirms the fact that is discussed before, namely, the ClGaPc molecules do not interact with the HOPG substrate. Further, it is clear that the Ga $2p_{3/2}$ peak position remains unchanged irrespective of the molecular orientation. It is only the strong molecule–substrate interaction due to the charge transfer from the substrate to the molecule or/and some chemical interaction through the Ga atom of the ClGaPc molecules that can shift or split the Ga $2p_{3/2}$ core-level spectra as observed in the ClGaPc/Au films.

A small spectral asymmetry is observed in the Ga $2p_{3/2}$ spectrum of the AG 15 Å film (Figure 9), which indicates the presence of an additional low-intensity broad peak toward the low binding energy side (not fitted separately in the figure). The presence of this broad peak in the AG 15 Å film, but not after annealing or in other films, is likely to be related to the structural imperfection in the AG multilayered film on the HOPG substrate. To understand this issue better, the topographies of the AG and AN 15 Å ClGaPc/HOPG films, obtained from the AFM measurements, are shown in Figure 10. It is clear that in the AG condition, the ClGaPc molecules

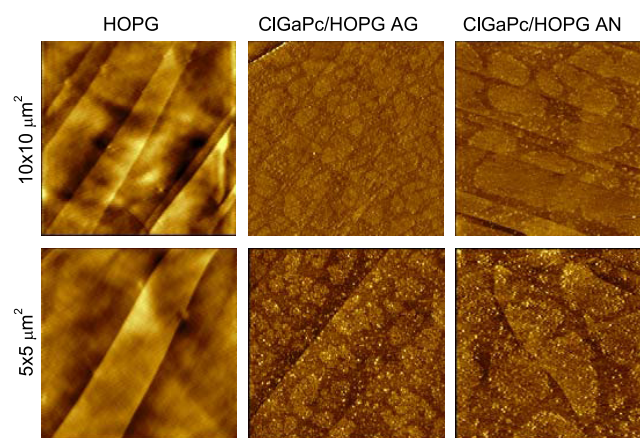


Figure 10. AFM images of the HOPG substrate and the 15 Å ClGaPc/HOPG thin film before (AG) and after (AN) thermal annealing, in two scan sizes, showing enhancement of the grain size with annealing.

form smaller islands of larger height (i.e., low coverage) on the HOPG surface, while after annealing they form larger islands of smaller height (i.e., higher coverage). The smaller-sized islands form a large grain-boundary area, which enhances the grain-boundary-related defects or disorders in the system, while the larger-sized islands reduce the grain-boundary-related defects or disorders in the system. It is thus confirmed that the small asymmetry in the Ga $2p_{3/2}$ spectrum of the AG 15 Å film is due to the grain-boundary-related defects or disorders, i.e., the structural imperfection in the AG multilayered ClGaPc/HOPG film.

4. OVERALL PICTURE AND SUMMARY

Let us now model the configurations and organizations of the ClGaPc molecules and draw the energy-level diagrams (ELDs) for the ClGaPc/Au and ClGaPc/HOPG interfaces before and after annealing for different film thicknesses to visualize the overall picture. The ELDs and the configurations of the ClGaPc molecules at the ClGaPc/Au and ClGaPc/HOPG interfaces can be modeled using the information obtained from

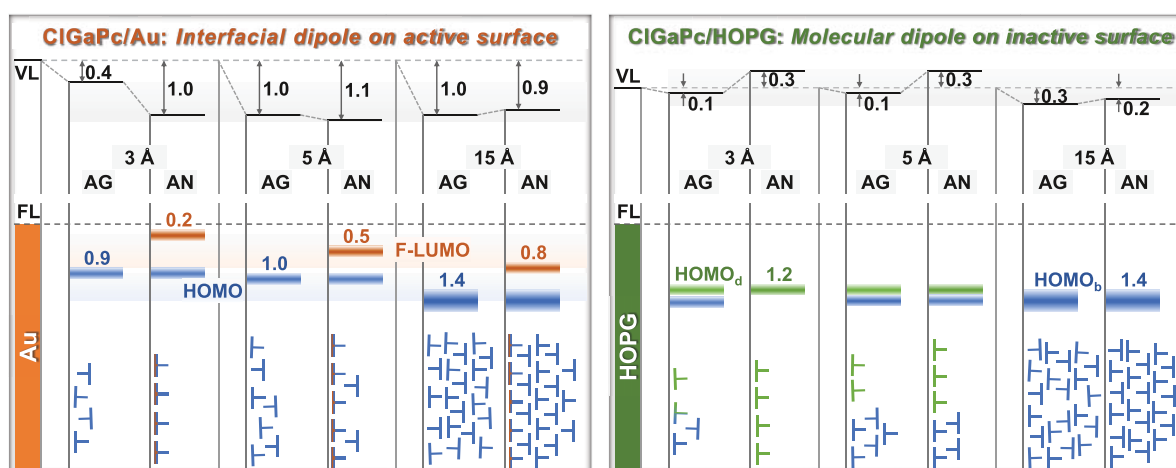


Figure 11. Energy-level diagrams of ClGaPc/Au and ClGaPc/HOPG thin films of different thicknesses before (AG) and after (AN) thermal annealing and their possible molecular configuration, organization, and interaction, as predicted from UPS and XPS measurements. The shift of VL, formation and evolution of the single HOMO level with or without the F-LUMO level in the ClGaPc/Au films, and evolution of HOMO_d and/or HOMO_b levels in the ClGaPc/HOPG films due to film thickness, coverage, configuration/orientation, organization, and substrate interaction of molecules are indicated.

the complementary UPS and XPS techniques, as shown schematically in Figure 11. The active nature of the Au surface and the inactive nature of the HOPG surface toward the ClGaPc molecules and thermal annealing are found to play important roles in the formation of different interesting ELDs, as discussed below. Thermal annealing provides thermal energy, which in general helps molecular reorganization and ordering through diffusion. Accordingly, some of the results observed here have been correlated to thermal-annealing-induced ordering and preferential orientation, following the analogy found in the literature for similar molecules.^{7–9,15,16}

The interfacial dipole moment, arising from the push-back, charge transfer, and molecular dipole induced effects, in the presence of interfacial interaction,^{4,6,41} seems to play a dominant role in charge reorganization on the active Au surface and deciding the VL of the ClGaPc/Au system. The coverage, configuration, and organization of molecules essentially decide such interfacial dipole moment and hence the VL. A small negative VL shift in the AG submonolayer film is due to the low coverage of mixed oriented and less organized ClGaPc molecules on the Au surface, while a large negative VL shift after annealing is due to an increase in the coverage of the well-ordered Cl-up oriented molecules in the presence of a strong Ga site-specific molecular interaction with the Au surface. A large negative VL shift in the AG sub-bilayer film is due to the large (actually maximum or full) coverage of mixed oriented and less organized ClGaPc molecules, while a negligible change in the VL shift after annealing is due to a small increase (possible) in the coverage of the well-ordered Cl-up oriented molecules in the first layer and the extra well-ordered Cl-down oriented molecules in the second layer. A similar large negative VL shift in the AG multilayer film is due to the similar structure, i.e., maximum or full coverage of mixed oriented and less organized ClGaPc molecules, while a small opposite change in the VL shift after annealing is due to the full coverage of the well-ordered Cl-up oriented molecules in the first layer and a similar full coverage of the well-ordered Cl-down oriented molecules in the second layer. An increase in the coverage of the well-ordered Cl-up oriented molecules decreases the VL level due to an increase in the push-back, charge transfer, and molecular-dipole-induced effects, which is

maximum for the monolayer film, while an increase in the coverage of the well-ordered Cl-down oriented molecules in the next layer neutralizes the molecular-dipole-induced effect more and more, which is prominent for the multilayered film.

The appearance of two bands in the HOMO region of the ClGaPc/Au films is well related to the above-mentioned structures. The band far away from the FL is the typical HOMO level, appearing from the collection of all of the molecules, irrespective of their configuration and organization, while the band relatively close to the FL is the F-LUMO level, appearing due to charge transfer from the active Au substrate to the well-ordered Cl-up oriented molecules through the Ga site-specific strong interaction. The thickness-dependent shift of the HOMO and F-LUMO levels is the typical band bending phenomenon observed on the metallic surface, which essentially suggests that the strong interaction or influence of the active surface is only toward the near-substrate molecules.

On the other hand, the effective molecular dipole moment, in the absence of interfacial interaction, seems to play a dominant role in deciding the VL of the ClGaPc/HOPG system. An increase in the coverage of the well-ordered Cl-up oriented molecules increases the VL level due to an increase in the molecular dipole effect,⁷ while an increase in the coverage of the bilayer (stacked) molecules (with Cl-up and Cl-down configurations) not only neutralizes such a molecular dipole effect through cancellation, as reported before,⁷ but also decreases the VL level, as evident here, probably due to the simple increase in the bilayer coverage, i.e., the coverage effect. Accordingly, a small negative VL shift in the AG submonolayer film is due to the mixture of less organized Cl-up oriented and bilayer molecules on the HOPG substrate, while a positive VL shift after annealing is due to an increase in the coverage of the well-ordered Cl-up oriented molecules on the HOPG substrate. Similar nature in the sub-bilayer film suggests that although the number of molecules increases, the ratio of the less organized Cl-up oriented and bilayer or bilayer-stacked molecules in the AG condition remains almost the same, while the presence of a bilayer, in addition to the increased well-ordered Cl-up oriented molecules, after annealing, makes the net molecular dipole moment almost the same as that of the sub-bilayer film. It can be noted that a monolayer film, covered

with well-ordered Cl-up oriented ClGaPc molecules (in absence of any bilayer) on the HOPG substrate, is expected to show a maximum positive VL shift, as shown before in the ClAlPc/HOPG system.⁸ A negative VL shift in the multilayer film is due to the coverage of the bilayer-stacked molecules (disorder or order) with a negligible net molecular dipole moment.

The appearance of two bands in the HOMO region of the ClGaPc/HOPG films supports well the above-mentioned structures. The band far away from the FL is the HOMO_b level, appearing from bilayer or stacked bilayer structures, while the band relatively close to the FL is the HOMO_d level, appearing from well-ordered Cl-up oriented molecules near the HOPG substrate having a definite molecular dipole moment. The intensity of each band is related to the amount of corresponding structures, and its variation with the film thickness is due to the variation in the amount of two structures. The absence of the HOMO_b level in the AN submonolayer film suggests a lack of bilayers in the film, while the absence of the HOMO_d level in the multilayer film suggests a lack of Cl-up oriented molecules near the substrate.

In summary, different energy-level diagrams are observed for the ClGaPc thin films adsorbed on the Au and HOPG substrates due to the different substrate surface activities. The molecular configurations of the monolayer film after annealing on both the substrates are however the same and seem to be well-ordered Cl-up orientation, which is quite interesting, as it certainly indicates a substrate-activity-independent energy minimum configuration. Thus, the active surface, depending upon its interaction, either repels to flip such a configuration to form a Cl-down orientation as reported on the Cu substrate¹⁶ (i.e., repulsive) or attracts further to maintain a well-ordered Cl-up orientation as predicted here on the Au substrate (i.e., attractive). The attraction or strong interaction gives rise to additional charge transfer and state transfer (of Ga) as evident from the formation of the F-LUMO level and low binding energy peak (P₁) of the Ga 2p_{3/2} core level. It is also evident that the difference between the vacuum and HOMO levels, i.e., the ionization potential (IP), for the predicted monolayer of well-ordered Cl-up oriented ClGaPc molecules on the Au substrate is minimum, while that on the HOPG substrate is maximum, although the ELAs of such monolayer on both the substrates are optimum, which is definitely another interesting consequence of substrate activity. Such interesting consequences are useful for tuning the charge transfer or charge injection, across the interfacial barrier, in organic semiconductor-based devices and make the present systems important, from the theoretical and further experimental point of view, for the calculation and verification of their electronic structures.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.0c12614>.

XPS calibration spectra and estimation of the vacuum level from the HBEC region of the UPS spectra of the ClGaPc/Au and ClGaPc/HOPG thin films (PDF)

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Notes

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