The effect of irradiation impinging on disparate anchoring configurations of polar-organic molecules adsorbed on bulk and thin-film metal surfaces

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The behavior of polar metal organic molecules, chloroaluminum phthalocyanine (ClAlPc), upon ultraviolet (UV) irradiation was investigated to evaluate the stability of the adsorption process on the Ag(111) thin film and bulk crystal. Angle-resolved photoelectron spectroscopy (ARPES) was mainly employed to measure the molecular energy states (MES) and vacuum level (VL) shift for 1-ML ClAlPc in the Cl-down configuration. A consistent trend was observed showing that ClAlPc in the Cl-down configuration is energetically more stable on the Ag thin-film surface than on the corresponding surface of the Ag bulk crystal. The intermediate adsorption state in tilted configuration during the irradiation impinging is identified by large positive VL shifts and broad spectra line shapes to infer a flipping mechanism from Cl-down to Cl-up configuration. Strain on the Ag thin films from the underlying mismatched Ge(111) substrate is considered to cause enlarged hollow sites on the Ag(111) thin-films, that anchor the Cl-down configuration more tightly on the thin-film surfaces, as confirmed by density functional theory (DFT) calculations.

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I. INTRODUCTION

Organic materials have been adopted extensively in the past two decades in electronics and optoelectronics applications such as organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), organic solar cells, and organic photovoltaic (OPV) devices. Developing and improving molecular devices using a broad variety of organic molecules [1-7] thus has become an area of research that sparked tremendous interest in the academic and industrial community. Generally, Metal-Phthalocyanine's (MPcs) are important for organic electronics because of their remarkable stability and specific ligand functionality towards metal electrodes. Polar MPcs, i.e. Chloroaluminium Phthalocyanine (ClAlPc), have received much attention due to its applications in electronic devices [8, 9], especially as its two different adsorption configurations, Cl-up

and Cl-down (see Figure 1), allow the tuning of the energy level alignment (ELA) that is crucial for charge-transport performance [10]. Manipulation of the dipole-up and dipole-down configurations of polar MPcs has shown to be possible by choosing different growing conditions or experimental techniques [11-13]. Lin et al. [13] successfully correlated the MES obtained by photoemission spectroscopy to the density of states (DOS) for the Cl-up and Cl-down configurations of ClAlPc. It was also demonstrated that the dipole orientation of the first ClAlPc layer can be controlled by adjusting the deposition rate and post annealing conditions with the ELA of the two adsorption modes of ClAlPc differing by ~ 0.4 eV.

With an Al-Cl unit generating a permanent dipole moment of 3.7 Debye for an isolated ClAlPc molecule in gas phase [14], the two different adsorption modes, i.e. Cl-up and Cl-down, of ClAlPc lead to distinct surface properties related to specific adsorption modes. For example, the VL shifts with respect to the Ag(111) work function are significantly different (Fig. 2(a) of Ref. 13). As illustrated in Fig. 1, for the Cl-down configuration, the VL shift is influenced by the Al-Cl molecular dipole as well as the Cl-Ag interfacial dipole that in view of the large differences in electronegativity [15, 16] between Cl (3.16) and Ag (1.93) is expected to be strong. For the Cl-up configuration, the VL shift is mainly influenced by the Al-Cl molecular dipole and the push-back effect [13] originating from the large interaction area of the phthalocyanine (Pc) plane and the Ag(111) surface [11, 17]. Another important aspect for both configurations is the adsorption stability. According to DFT calculations [13], ClAlPc has an adsorption energy of -3.56 eV in Cl-down configuration and of -5.22 eV in Cl-up configuration. While the latter can be attributed to the stabilizing interaction of the Pc molecule with the substrates surface, it is still possible to form a monolayer (ML) mainly consisting of Cl-down configuration on Ag(111) *via* a very slow deposition rate [13]. Hollow sites among Ag(111) atoms were considered important for the formation of the metastable Cl-down ClAlPc layer [13]. Therefore, it is physically interesting to investigate how the Cl-down configuration responds to any change of the substrate properties and intended perturbations. In this paper we employ two approaches: first, by using either a Ag film of different thickness or a Ag bulk crystal as the substrate and second, by using UV radiation light as the perturbation source. Due to the lattice mismatch with the substrate of Ge(111), there are strain effects to be expected within the Ag thin film [18, 19]. In this case, the increased Ag-Ag distance of the surface atoms imposes a larger hollow site, which in turn allows the Cl atom of the Cl-down configuration to anchor deeper, providing further energetic stabilization. In contrast, on the Ag(111) bulk surface, the Cl-down configuration is expected to have disparate energetic stability. The energy and pressure inflicted by irradiation impinging to the ClAlPc molecule can further probe the adsorption stability. We have measured and analyzed the dependence of photoemission line shapes of the MES and VL shifts of 1-ML Cl-down ClAlPc on photon flux and exposure time. We indeed found that the Cl-down configuration of ClAlPc is more stable on the Ag thin-film than on the Ag bulk crystal surface. The explanation for this finding seems to be related to the Ag bond strain imposed by Ge(111) and is provided with the assistance of DFT calculations. In addition, an anchoring mechanism of ClAlPc in the Cl-down configuration is proposed upon irradiation impinging.

II. EXPERIMENTAL PROCEDURES AND METHODS

A N-type Ge(111) wafer and a bulk Ag(111) crystal were chosen as starting substrates for ClAlPc. The clean substrates were achieved by standard sputtering and annealing procedure and confirmed by sharp low-energy electron diffraction (LEED) unveiling the Ag(111)- 1×1 and the Ge(111)-c(2×8) patterns. Ag

films of 7, 9 and 16 ML were deposited onto the clean Ge(111) substrate at around 130 °C to 140 °C, followed by annealing at ~35°C to attain the uniform films [13, 20]. The thickness of Ag films was determined by the calibrated thickness-depended energy positions of Ag quantum-well states (QWS) [13, 20]. ClAlPc molecules were thermally deposited onto surfaces of Ag films and the bulk Ag(111) at the room temperature. The deposition rate was determined by the precalibrated quartz thickness monitor. We found that for forming 1-ML ClAlPc in Cl-down configuration on Ag films and the bulk Ag(111), the optimal deposition rates are 0.1 and 0.04 Å/min, respectively. 1-ML ClAlPc was determined by the coverage-dependent VL shift and further calibrated by the photoemission intensity ratio between ClAlPc MES and Ag substrate states [13]. ARPES experiments were carried out with 50-eV photons and the photon fluxes were controled by the slit and measured by the mesh currents at the 08A1-LSGM beamline of the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. Based on the previously calibrated relation between the photon flux and the mesh currents, the photon-flux values were determined. The energy resolution of the ARPES system is 50 meV and the spectra of the Ag(111) surface Brillouin zone was taken along the Γ M symmetry direction. The sample was electrically biased at normal emission 6.0 V to obtain the VL shift [20] in order to shift the secondary cutoff into an energy range suitable for detection by the electron analyzer.

The ab-initio calculations were performed using the Vienna Ab-initio Simulation Package (VASP) [21-23] based on density functional theory (DFT). The Perdew–Burke–Ernzerhof (PBE) [24] generalized-gradient-approximation functional, and the projector augmented wave (PAW) [25, 26] method are employed in the self-consistent calculations. The ClAlPc/Ag(111) system is simulated by putting a ClAlPc molecule on top of the Ag(111) 6x6 supercell with the thickness of 3 Ag layers. The Ag(111) 6x6 supercell adopted here is approximately the smallest one that can accommodate the ClAlPc molecule without imposing steric effects. By adjusting the lattice constant of the Ag substrate from 4.09 to 4.40 Å, we study the evolution of the energy change of ClAlPc with both the Cl-down and the reversed Cl-up orientation. For each case, we fixed the lattice constant while the atomic positions were optimized until the total energy converges within 10^{-4} eV. The plane-wave cutoff energy is set at 400 eV on 6x6x1 k-mesh over the 2D Brillouin zone.

III. RESULTS AND DISCUSSION

The photoemission spectra in Figures 2(a)-2(c) show a series of energy distribution curves (EDCs) for a step-by-step incremental deposition of ClAlPc onto Ag films of 7 and 9 ML deposited on Ge(111), and a single bulk Ag crystal surface. For ClAlPc on Ag films, a single peak located at 9.70 eV emerges and increases in intensity up to 1 ML ClAlPc. As was demonstrated in a previous study [13], this peak (previously measured at 9.71 eV) represents the MES of the Cl-down configuration. The peak for ClAlPc on a bulk Ag crystal surface turns out to be different; the emerging peak is a lot broader and the energy position of -8.92 eV is closer to that for a Cl-up configuration (previously measured at 8.76 eV) [13]. The broadness of the peak and the shifted energy, however, indicates that the peak might result from more than a single molecular configuration.

Figure 2(d) shows the corresponding coverage dependence of the VL shifts for the cases in Figs. 2(a)-2(c). As can be seen, the VL shifts for ClAlPc deposited on the bulk Ag crystal are larger than those on Ag films. This is in contrast to the previous observation that VL shifts for Cl-up configuration are lower than

those for Cl-down configuration (Fig. 2(a) of Ref. 13). This finding points towards the presence of an intermediate configuration between Cl-up and Cl-down. The only configuration that fulfills the observed VL shift requirements is a tilted configuration, with a surface interaction between that of Cl-down and Cl-up.

The ClAlPc deposition rates for ClAlPc on Ag films and the bulk Ag(111) crystal surface are relatively low and very similar in all cases so they are unlikely to be the cause of the observed differences in spectra. Due to the fact that the collected coverage-dependent photoemission data set in Figs. 2(a)-2(c) undergo elongated exposure for hours to the irradiation, the adsorption configurations of organic molecules, especially those in a metastable state, could alter over exposure time. In other words, the stability of the absorbed molecules can be examined by the irradiation effect. Figures 3(a) and 3(b) show a series of time-dependent photoemission spectra of 1 ML ClAlPc in Cl-down configuration deposited on 7-ML Ag thin film and a Ag bulk crystal surface, respectively under radiation exposure with a flux of 3.15×10^{13} photons/s. The evolution of the peak line shape within the energy range of 10 eV to 9.8 eV is evident; for both cases, the peaks decay in intensity and shift toward higher energy. The final curves after 50 min of radiation exposure (black) were fitted using two Lorentzians representing the Cl-up (green, centered at 8.6 eV) and the Cl-down (amber, centered at 9.7 eV) configuration, and a smooth polynomial background (grey). As seen, for ClAlPc on 7-ML Ag film, the peak line shape still shows Cl-down component (amber) dominates but for ClAlPc on bulk Ag(111) crystal surface, the Cl-up component (green) has the same intensity as that of the Cl-down component. This explains the results of Figure 2; after prolong radiation exposure, ClAlPc stays mainly at Cl-down configuration on Ag thin films, but partially evolves to Cl-up configuration on bulk Ag(111) crystal. Figure 3(c) shows a series of time-dependent photoemission spectra of 1 ML ClAlPc on bulk Ag(111) crystal with the reduced photon flux of 2.11×10^{13} photons/s. The fitting to the peak of the last EDC still exhibits the equal composition of both configurations, namely, the same intensity of the two fitting Lorentzians, but the line widths are obviously narrower than those in Fig. 3(a). This implies that more amounts of ClAlPc molecules in the intermediate state between Cl-down and Cl-up are produced under more-intense radiation exposure since the tilted configuration can be regarded as the incomplete one of either the Cl-up or Cl-down; the corresponding MES peaks shift away from the original positions of both configurations to cause the broadening. The measured VL shifts upon radiation exposure for the three cases in Figs. 3(a)-3(c) are 0.28, 0.37, and 0.48 eV, respectively. As shown in Fig. 1, the contributions to the positive VL shift of the Cl-down configuration originate from the Cl-Ag interfacial dipole. For the Cl-up configuration, the push-back effect dominates the negative VL shift of the Cl-up configuration. The question remains, however, why the measured VL shifts are positive and large for all the cases of Figs. 3(a)-3(c), where parts of Cl-down ClAlPc molecules were driven to the Cl-up configuration by irradiation impinging? We believe there is an intermediate state of tilted configuration for Cl-down ClAlPc to flip to Cl-up one during the irradiation impinging, as depicted in Fig. 3(d). Scanning tunneling microscopy (STM) [27-30] indicated that the tunneling of the Cl atom through the Pc plane is the most energy-efficient way for the switching between the Cl-down and the Cl-up configuration. But, in our case, the impinging photons don't just carry energy but also impose radiation pressure into the molecules, so the anchoring point for a Cl atom on Ag surface may work as a rotational pivot for the flipping. The radiation pressure derived from the photon fluxes employed in Fig. 3(b) and 3(c) are 8.42×10^{13} and 5.64×10^{13} N/m², respectively. When the Cl-down ClAlPc is tilted, the VL would increase based on two possible reasons: First, the vertical component of the molecular dipole length decreases due to the tilted angle as shown in Fig. 3(d) so the

negative contribution to the VL shift from the Al-Cl molecular dipole moment would be correspondingly reduced, and the total VL shift, which is the sum of negative contribution from molecular dipole and positive contribution from interfacial dipole (illustrated in Fig.1), would increase. Second, due to the irradiation impinging, the molecular dipole would be deformed so that the Cl-Al bond becomes weaker, leading to even more charge transfer to Cl atom to cause larger positive VL shift than the case of Cl-down configuration.

To further confirm this picture, we investigate the irradiation effect on 1-ML ClAlPc/Ag(111) bulk crystal for the two following cases: Cl-down and Cl-up configurations coexisting (see Fig. 4(a)) and Cl-down configuration dominating (see Fig. 4(b)). For the first case, the EDC line shape in the beginning exhibits two distinct peaks; one for Cl-down at 10.48 eV and one for Cl-up at 9.05 eV. Note that the different energy positions of these peaks from those of single Cl-down and Cl-up peaks, 9.7 eV and 8.6 eV, are due to the change of ELA. As shown in the sketch of coexisting configurations for ClAlPc at the top of Fig. 4(a), Cl-down and Cl-up ClAlPc should anchor side by side to ensure stability by the attraction force between opposite dipole moments [31]. With this type of arrangement, Cl-down ClAlPc is less likely tilted or even flipped upon irradiation impinging than the second case of Cl-down dominating configuration. However, after 50-min radiation impinging, the peak shape shows almost a complete Cl-up peak for the first case as shown in the middle part of Fig. 4(a), inferring mainly the tunneling mechanism to switch from Cl-down to Cl-up configuration. The middle part of Fig. 4(b), the second case, shows the EDC for 1-ML Cl-down ClAlPc on bulk Ag(111) crystal after 50-min radiation impinging. The peak line shape is a lot broader, manifesting disordered tilted configuration. The measured VL shifts after 50 min radiation impinging in the first and second cases are 0.14 and 0.37 eV. The much larger positive increase of VL shift for the latter case is in line with the picture depicted in Fig. 3(d). In both cases, annealing at 60 C for 30 min was carried out after irradiation. As seen from the bottoms of Figs. 4(a) and 4(b), Cl-up peak is shaper with VL shift of 0.1 eV in the first case, but the broad peak in the second case become even broader with VL shift of 0.05 eV, indicating a more complete Cl-up configuration and the robustness of the tilted configuration, respectively.

Since Cl-down configuration is more stable on Ag thin films than on bulk Ag(111) crystal, it is very interesting to further investigate the stability dependence on the thickness of Ag thin films. Figure 5(a) shows the EDCs taken at normal emission for a clean bulk Ag(111) crystal surface, and 7-, 9-, and 16-ML Ag films grown on Ge(111). For the bulk Ag(111) crystal surface, the main features are a sharp Shockley surface state (SS) about -0.1 eV and a broad bulk edge near -0.3 eV [32]. For Ag thin films, in addition to the surface states, a series of QWS peaks marked with different quantum numbers ν 's in the EDCs characterize the Ag thickness with their energy positions [20, 33, 34]. The comparison between EDCs before (dashed curves) and after (solid curves) 50-min irradiation impinging with the flux of 3.15×10^{13} photons/s for 1-ML Cl-down ClAlPc on the bulk Ag(111) crystal and Ag thin films are presented respectively in Fig. 5(b). It is noteworthy that the initial energy positions for the Cl-down peaks are different, as marked in Fig. 5(b), as the initial anchoring is not settled. After irradiation impinging, the Cl-down peaks of all the cases shift to the positions near -9.7 eV as indicated by the vertical dashed line, but the line widths become broader for the bulk Ag(111) crystal and 16-ML Ag film than the 7- and 9-ML Ag films. The enhancement of the shoulder at about -3.8 eV for the former, mainly representing the partial DOS from Cl for Cl-up configurations [13], also indicate that some Cl-down ClAlPc molecules flipped to a Cl-up configuration. We

further fitted the peak line shapes during irradiation impinging with two Lorentzians representing Cl-down and Cl-up components and plot the intensity of the two components versus exposure time in Fig. 5(c) and Fig 5(d). The time dependence of the peak component intensity was approximated by $I = \pm I_0 \exp(t/\tau) + c$, where τ is the time constant and c is an offset constant. Positive and negative signs of the exponential function are for the decrease of the Cl-down and increase of Cl-up components, respectively. For the decay of the Cl-down peak, the extracted time constants are, $\tau = 27.7, 17.7, 16.69$, and 11.14 mins for ClAlPc on 7- and 9-ML, 16-ML Ag films and bulk Ag(111) crystal surfaces, and for the growing of Cl-up peaks are $23.25, 12.98, 11.76$, and 10.92 mins. Therefore, the higher stability of the Cl-down configuration on thinner Ag films is evidently indicated by the larger time constant for both the Cl-down and the Cl-up configurations. In addition, the rougher surface of 16-ML Ag film/Ge(111) as indicated by the low and broadened SS and QWS in Fig. 5(a) has closer adsorption stability to the uniform bulk Ag(111) surface, ruling out the surface defect or roughness as the effective factor for the adsorption stability.

Figures 6(a) and 6(b) show the LEED patterns of a clean Ag(111) bulk crystal surface and a 7-ML Ag thin film, respectively. The lattice mismatch between Ag(111) and Ge(111) is 28% in terms of their bulk lattices ($a_{\text{Ag}} = 4.08 \text{ \AA}$, $a_{\text{Ge}} = 5.66 \text{ \AA}$) when their symmetry axes are aligned with each other. Therefore, the Ag thin films growing parallel to Ge(111) would be subject to tensile strain effects that enlarge the sizes of the hollow sites between Ag atoms, which have been observed to be the anchoring positions for Cl-down ClAlPc molecules on Cu(111) [35]. As observed, the LEED spots of the Ag film with arc shapes are indeed much broader than those of the bulk Ag(111) crystal surface but the spot positions are about similar, indicating that the actual tensile strain exerted on the Ag films is a lot smaller than 28%. The arc lengths indicate a mosaic structure of films rotating over a certain range and this was considered as a spontaneous mechanism for reducing large lattice mismatch [36,37]. It is noteworthy that the same LEED-spot shape was also observed from a strained Ag film on the lattice-mismatched Si(111) substrate, and the strain effect was used to explain the disappearance of the surface state of the Ag film [38]. We carried out the DFT calculations for the Cl-up and Cl-down configurations on Ag slabs with varied lattice constants ranging from $4.09 \text{ \AA}$, near the bulk counterpart, to $4.40 \text{ \AA}$. Figures 7(a)-7(c) show the top and the side views of the model layouts for the calculation. The resulting total energy for Cl-up and Cl-down configurations are exhibited in Fig. 7(d): The key results to be taken from this graph is that upon lattice increase from Ag bulk lattice, the energy of the system increases slower for the Cl-down than for the Cl-up configuration, with a crossover of the two configurations being observed at about $4.3 \text{ \AA}$. To isolate the effect of the relative orientation, we subtract the total energy of Cl-up from that of Cl-down configuration as shown in Fig. 7(e) (as the difference between the total energy of both configurations approximately cancels out the contribution from the Ag slabs). The overall descending behavior with the increasing Ag lattice is indicated by the fitting line with negative slope. So the take home message is that the Cl-down configuration starts more stable, right when the tensile strain on the Ag lattice increases from zero.

IV. SUMMARY

In conclusion, by analyzing the photoemission spectra line shape of MES and VL shifts, we investigated the time-dependent behavior of Cl-down ClAlPc under irradiation exposure. It was observed that it anchors more stably on Ag thin films than on the bulk Ag(111) crystal surface, and a description of how the transition from Cl-down to Cl-up configuration occurs was presented. Unlike thermal energy, incident

radiation does not just inflict energy but also pressure to the Cl-down ClAlPc molecule so it would tend to flip with the tilted configuration at the intermediate stage as revealed from the large increase of VL and broad spectra line shape. This is different from the tunneling mechanism suggested by STM that switches between Cl-down and Cl-up configuration of the ClAlPc molecule by applying negative and positive bias voltage from the STM tip [28], with potential application to molecular digital memory [27]. Our probing of the switching mechanism via irradiation gains deeper insight. Specifically, the irradiation-impinging effect we discovered can be employed to modify the adsorption configurations of other functional molecular dipoles for various purposes, initiating a new direction in terms of the impact of irradiation on polar organic molecules. The higher stability of Cl-down ClAlPc on Ag thin films is attributed to strain effects due to a large lattice mismatch, between the Ag thin film and underlying Ge(111) substrate. Our results are in line with DFT calculations based on a slab model of the Ag(111)/ClAlPc interface for different lattice constants. This finding provides a new avenue that may enhance the controlled fabrication process of organic optoelectronic devices at the nanoscale. In addition, we expect our results to initiate further advanced studies of relevant irradiation effects, such as photon-energy dependence, on the adsorption of polar-organic molecules.

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Figure captions:

FIG. 1. The schematic illustration of ClAlPc molecules adsorbed on a Ag surface in Cl-down and Cl-up configurations with two types of dipole formation indicated. .

FIG. 2. Coverage dependent angle-resolved photoemission spectra of ClAlPc on (a) a 7-ML Ag film, (b) a 9-ML Ag film (c), and a Ag(111) bulk crystal surface. (d) VL shift as a function of ClAlPc coverage on a 7-ML Ag film, a 9-ML Ag film, and a Ag(111) bulk crystal surface. Blue and green colors of EDCs denote the ClAlPc at the coverage of 0 and 1 ML ($3.5\text{\AA}$).

FIG. 3. Time-dependent angle-resolved photoemission spectra of 1 ML ClAlPc on (a) a 7-ML Ag film and (b) a Ag(111) bulk crystal surface undergoing irradiation impinging at the photon fluxes of 3.15×10^{13} photons/s. (c) The same as (b) but with the photon fluxes of 2.11×10^{13} photons/s. The amber and green curves indicate the fitting components of Cl-down and Cl-up configurations. The grey curve indicates the fitting background. The red dashed curve indicates the total fitting result. The energy positions of the Cl-down peak before irradiation impinging are marked with the vertical dashed lines. (d) The schematic model to illustrate the flipping process from Cl-down to Cl-up configuration under irradiation impinging.

FIG. 4. Angle-resolved photoemission spectra of 1-ML ClAlPc on Ag(111) bulk crystal before and after irradiation, and after subsequent annealing for (a) coexisting Cl-down and Cl-up configurations and (b) dominant Cl-down configuration. The arrows indicate the energy positions of peak maximums.

FIG. 5. Angle-resolved photoemission spectra of EDCs for (a) 7-, 9-, 16- ML Ag films on Ge(111), and the Ag(111) bulk crystal surface, and (b) 1-ML Cl-down ClAlPc before (dashed curves) and after (solid curves) radiation impinging on 7-, 9-, 16-ML Ag films and the Ag(111) bulk crystal. The vertical dashed line indicates the energy position of -9.7 eV. (c) & (d) Intensity as a function of radiation exposure time for Cl-down and Cl-up components.

FIG. 6. LEED patterns of (a) a Ag(111) bulk crystal surface and (b) a 7-ML Ag thin film on Ge(111), taken at the electron energy 50 eV.

FIG. 7. Lattice structure, total energy, and out-of-plane charge profile of ClAlPc/Ag(111). (a) Top view and (b) side view of the ClAlPc molecule on top of Ag(111) 6×6 supercell with the Cl ion heading up (Cl-up). (c) Side view of the ClAlPc molecule on top of Ag(111) 6×6 supercell with the Cl ion heading down (Cl-down). (d) Total energy of the supercell with Cl-up and Cl-down orientations as functions of Ag lattice constant from $4.09 \text{ \AA}$ (single bulk crystal) to $4.40 \text{ \AA}$ (film). (e) Difference in total energy of Cl-up and Cl-down configuration

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7