Here, we investigated the relationship between the surface potentials and molecular interactions in the alucone films grown by molecular layer deposition. Varying the C–C bond order of the organic precursors induced variations in inter-molecular interactions, resulting in variation in the surface potential, associated with the work function of the films.

The unwaning interest in thin-film electronic devices is fueled by their potential for application in organic electronics. Many attempts have been made to improve the device function and performance, including the carrier mobility and the light out-coupling efficiency. The work function of the organic layers is crucial for energy level alignment and is quite sensitive to the surface potential, which is a function of the chemical identity of a material, and molecular orientation. These factors, especially those related to the contact area, reportedly lead to a non-uniform electrostatic potential even on an ostensibly uniform surface. This non-uniformity in the work function is known to affect the device performance, including the sub-threshold swing and turn-on voltage. Therefore, it is essential to precisely control and uniformly retain the surface potentials of organic thin-films to reduce variations in the work function caused by random orientation at the contact area and grain boundary.

Generally, polymeric thin films have been fabricated by using the solution-based conventional methods, but they have some limitations of the conformal coating of nanostructures and the control of molecular orientation. To improve the conformal coating of polymeric films, it is essential to introduce gas-phase approaches, including chemical vapor deposition (CVD), vapor deposition polymerization (VDP), and molecular layer deposition (MLD). Among these methods, MLD is based on the sequential and self-limiting surface reaction to form conformal and ultrathin polymer films at the molecular level. Recently, it was reported that the intra- and intermolecular interactions in MLD films influence the adhesive, thermal, and optical properties of the molecular layers. The molecular flexibility and \( \pi-\pi \) interactions between adjacent aromatic rings enhanced the intra- and intermolecular interactions, resulting in double reaction, and molecular alignment, respectively. For these reasons, many researchers have focused on controlling the molecular interactions by tailoring various aspects of the MLD growth process and suggested various applications of coating technology. However, the relationship between the electrical properties and the molecular interactions in the films has still not been clearly elucidated.

In this study, we explored the molecular interaction-dependent surface potentials in ultrathin and conformal organic–inorganic alucone films grown by MLD. These films are fabricated using trimethyl aluminum (TMA) and diols with different C–C bond order (1,4-butanediol, BDO or 2-butyne-1,4-diol, BYDO) as inorganic and organic precursors, respectively. The mass gains of the alucone films that occur with sequential doses of TMA and organic diols are monitored by using an in situ quartz crystal microbalance (QCM). The growth behaviors and surface potentials are probed by ellipsometry and scanning Kelvin probe microscopy (SKPM), respectively. Further, all molecular geometries and energies are predicted by performing density functional theory (DFT) calculations.

The hybrid organic–inorganic alucone thin films were fabricated by using a homemade MLD chamber with an in situ QCM system (Fig. S1 and Table S1, ESI†). The alucone MLD films were grown on Si(100) wafers at 90 °C via sequential surface reaction of the inorganic and organic precursors to obtain \( \text{O-Al-O-(CH}_2\text{)}_m \text{)} n \) polymeric films as shown in Fig. 1a. The self-limiting reactions of BDO and BYDO with TMA at the surface were optimized by monitoring the thickness profiles as a function of the dose time (Fig. S2, ESI†). We also investigated the growth behavior of [TMA/BDO] n alucone MLD films as a function of the number of MLD cycles by varying the temperature of the BDO precursor (Fig. 1b). When the temperature of BDO was increased from 50 to 60 °C, the growth rate increased from 3.1 to 4.6 Å per
Fig. 1 (a) Schematic diagram for the growth of hybrid organic–inorganic alucone MLD films using TMA and diols (BDO and BYDO) with different C–C bond orders. Growth behaviors of (b) (TMA/BDO)$_n$ alucone MLD films versus the number of MLD cycles with variation of the BDO precursor temperature, and (c) thickness profiles of (TMA/diol)$_n$ alucone MLD films as a function of the number of MLD cycles. The dotted line represents the ideal line based on <150 initial deposition cycles. Mass gain curve of (d and e) (TMA/BDO)$_n$, and (f and g) (TMA/BYDO)$_n$, alucone MLD films for (d and f) early (16 to 20 cycles) and (e and g) late (250 to 255 cycles) stage.

We attribute this high growth rate to the increase in the vapor pressure with high kinetic energy and concentration of the precursors, caused by the increase in the temperature of BDO. Fig. S3 (ESI†) shows that both alucone MLD films have a homogeneous surface with BDO temperature change, which indicates that there is no difference in coverage. The thickness of the (TMA/diol)$_n$ alucone MLD films was monitored as a function of the number of cycles due to intramolecular interaction of the BDO precursors. However, for the (TMA/BYDO)$_n$ alucone MLD film, the slope of the mass gain profile remained nearly constant through 300 cycles with molecular ratios of 1:0.70 and 1:0.65 in the early and late stages, respectively, indicating constant growth behavior throughout the MLD cycles shown in Fig. 1f and g. We attribute this constant growth behavior of the (TMA/BYDO)$_n$ film to the rigidity of the triple C–C bond in the BYDO precursor.

To estimate the geometry and orientation of the molecules in the (TMA/diol)$_n$ alucone MLD films, a molecular model was designed with (TMA/diol)$_n$ couples covalently bonded at the two most stable sites on the Si(100) substrate (Fig. S6, ESI†), and density functional theory (DFT) calculations were conducted, as shown in Fig. 2. The calculation results show that the average height of (TMA/BDO)$_n$ and (TMA/BYDO)$_n$ on the Si(100) substrate were 7.54 and 7.45 Å, respectively, and their molecular orientations were quite different. For (TMA/BDO)$_n$, there was no molecular interaction with the lateral layer. However, the...
calculated geometry of (TMA/BYDO)$_n$ shows that the adjacent carbon chains of the BYDO precursors were parallel to each other, and a vertical structure with resonance stabilization by π–π interaction is preferred, with a distance of 3.52 Å between adjacent carbon chains with triple bond order. The calculated height of (TMA/BDO)$_n$ is slightly larger, but (TMA/BYDO)$_n$ is larger at the growth rate due to the molecular orientation, which means that the aforementioned π–π interaction between carbon chains could lead to uniformly aligned molecular orientation and constant growth behavior of the (TMA/BYDO)$_n$ alucone film, which corresponds to the results presented in Fig. 1c, f and g. In addition, we conducted the FTIR measurement of the (TMA/diol)$_{300}$ alucone MLD films, and compared the full width at half maximum (FWHM) values of CH$_2$ peak to analyze the peak broadness, resulting from inter-molecular interaction of organic molecules (Fig. S7, ESI†). The FWHM values were 123.69 and 97.33 cm$^{-1}$ for (TMA/BYDO)$_{300}$ and (TMA/BDO)$_{300}$, respectively. It also supports that the intermolecular interaction in (TMA/BYDO)$_{300}$ is more stronger than one in (TMA/BDO)$_{300}$, inducing the formation of more aligned (TMA/BYDO)$_{300}$ film.10

AFM images and line profiles of the (TMA/diol)$_{300}$ alucone MLD films were acquired to investigate the correlation between the surface morphology and the molecular interaction. As shown in Fig. S8 (ESI†), the surface of the (TMA/BYDO)$_{300}$ film was relatively smooth with a root-mean-square (RMS) roughness of 0.181 nm, whereas black holes were observed in the AFM image of the (TMA/BDO)$_{300}$ films.13 Fig. S9 (ESI†) shows the DFT calculations of potential energy required for the double reactions, indicating that BDO has a lower potential energy than BYDO. We believe that this lower value for BDO enhanced the intra-molecular interactions such as the double reaction, which led to a loss of reaction sites,27 and the formation of holes in the (TMA/BDO)$_n$ alucone MLD films.

To investigate the molecular interaction-dependent surface potentials, we conducted SKPM measurement of the (TMA/diol)$_n$ alucone MLD films. Considering the potential sources for changing of surface potential, such as surface roughness, physisorbed particles, air, humidity, and unexpected molecular bindings, we measured immediately the surface potential of relatively smooth part in alucone MLD films after AFM measurement, as shown in Fig. S10 (ESI†). The mapping images of the surface potentials for the (TMA/diol)$_n$ alucone MLD films and the corresponding line profiles and histograms are presented in Fig. 3 (Experimental details, ESI†). At 0 V sample bias, the average surface potentials of the (TMA/BDO)$_{100}$ and (TMA/BYDO)$_{100}$ alucone MLD films were 0.598 and 0.471 V with standard deviations of 0.248 and 0.048 V, respectively. Upon shifting the bias voltage from 0 to 3 V, the surface potentials increased correspondingly, which shows that the electrical properties of the alucone MLD film did not change with the applied voltage. However, the standard deviation for the (TMA/BDO)$_{100}$ film was still five times larger than that for the (TMA/BYDO)$_{100}$ film, as shown in the line profiles and histograms of the surface potential (Table S2, ESI†). Furthermore, as the number of cycles increased from 100 to 300, the standard deviation for the (TMA/BYDO)$_{300}$ film was constant at 0.048 V, whereas, in the case of the (TMA/BDO)$_{300}$ film, the standard deviation increased from 0.248 to 0.327 V. These results support that the molecular misalignment in the (TMA/BDO)$_n$ alucone MLD films was enhanced by increasing the number of cycles, resulting in the generation of charge trap site. Furthermore, it can be enhanced to diffuse TMA molecules into the alucone MLD films,28 which can affect cross-linking reaction between molecular layers and potentially cause surface potential changes. We attribute the above homogeneous and narrow distribution of the surface potential in the (TMA/BYDO)$_n$ films to inter-molecular interactions, such as π–π interaction, during film growth. This interaction could lead to

Fig. 3 Two-dimensional SKPM images, line profiles, and histogram of (a) (TMA/BDO)$_{100}$, (b) (TMA/BYDO)$_{100}$, (c) (TMA/BDO)$_{300}$, and (d) (TMA/BYDO)$_{300}$ alucone MLD films at 0–3 V. The scan area of each image is 4 μm × 4 μm.
uniformly aligned molecular orientation, and suppress the local distribution of charge traps among molecular layers.

Based on the SKPM measurement for [TMA/diol]$_n$ and the highly oriented pyrolytic graphite (HOPG) as a standard sample, we calculated and compared the work functions of the (TMA/diol)$_n$ films, demonstrating a strong correlation with the surface potential (Experimental details, ESI†). When the MLD cycle was increased from 100 to 300, the work functions of (TMA/BDO)$_n$ increased from 4.149 to 4.199 eV, whereas that of (TMA/BDYD)$_n$ was nearly constant (4.278 vs. 4.275 eV, respectively) in Table S3 (ESI†). Strong inter-molecular interactions could form well aligned molecular orientation during MLD growth and prevent the local formation of an open-structured polymer film, thereby reducing the generation of charge trap sites and leading to a low standard deviation. Thus, the aforementioned homogeneous distributions of the surface potential on (TMA/BDYD)$_n$ films are quite-reasonable, and correspond well with the growth rates, mass gain curves, and molecular geometries.

In summary, we investigated the molecular interaction-dependent surface potentials in (TMA/diol)$_n$ alucone films grown by sequential MLD growth of TMA and two diols with different C–C bond orders. Their self-limiting reactions and growth behaviors were confirmed by measuring the thickness profiles and mass gain curves using ellipsometry and QCM, respectively. DFT calculations were also performed to predict the molecular geometry of the (TMA/diol)$_n$ alucone films, and the molecular interactions were discussed, including the π–π interaction between triple carbon bonds that lead to uniformly aligned molecular orientation and a homogeneous surface potential with a low standard deviation. Furthermore, we demonstrated that the surface potentials and work functions are related to the molecular interactions based on SKPM measurement. If there are no molecular interactions, the polymer thin film adopts a more open structure with more charge traps. Therefore, we propose that the molecular interactions can influence the surface potential distribution. We expect that our findings on how to decrease the variation in the surface potential will contribute to improving the performance of nanoelectronic devices for controlling variations in the work function.

This work was supported by the Basic Science Research Program (2017R1E1A1A01075377) and the Medical Research Center Program (No. 2011-0030074) through the National Research Foundation (NRF) funded by the Ministry of Science, ICT & Future Planning.

Conflicts of interest

There are no conflicts to declare.

Notes and references