Nano Innovation 2024 Rome, 9-13 September
Conference & Exhibition

SAPIENZA UNIVERSITÀ DI ROMA

CNR Istituto di Struttura della Materia

Investigation of the electronic properties of Ru bis-Phthalocyanine Molecules on MgO/Ag(100)

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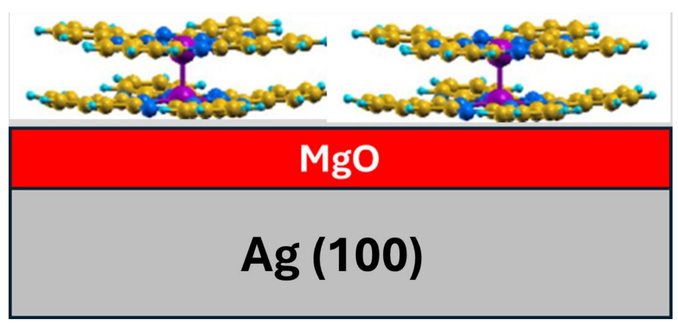
Abstract

When magnesium oxide (MgO) thin films are prepared on metal substrate, its properties are not so different from the bulk one. In this study, we prepared magnesium oxide (MgO) thin film on silver-Ag(100) surface and investigated the properties of ruthenium phthalocyanine (RuPc) molecules deposited on this substrate. Scanning tunneling microscopy (STM) revealed that MgO was grown epitaxially on Ag(100) with average island size of approximately 50 nm for less than 1 monolayer (ML). Scanning tunneling spectroscopy (STS) confirmed the presence of clean Ag patches in-between MgO islands. The bandgap of thin MgO film is comparable to bulk MgO. Deposition of 1ML of RuPc on MgO/Ag(100) has formed well ordered patterns on clean Ag patches and less ordered arrangements on MgO islands. A shift in molecular orbital is observed for RuPc on MgO/Ag(100) as compared to RuPc on clean Ag(100). After annealing, we were able to observe single RuPc molecules on MgO islands. Preparing a well-ordered surface with RuPc on MgO/Ag(100) is useful for many spin-based devices, sensing, catalysis and magnetic applications.



RuPc deposition on Ag (100)

RuPc deposited on Ag (100) usually form two types of well-ordered structures. One is low the density structure which is observed around 0.3 ML of RuPc and the second type is the high density one which is obtained around 1 ML[1]. In our study, more han 1ML of RuPc deposition has produced the expected high-density structure (a and c) as well as a novel 6x6 reconstruction (b) not reported in the literature which was confirmed by low energy electron diffraction (LEED) (d).

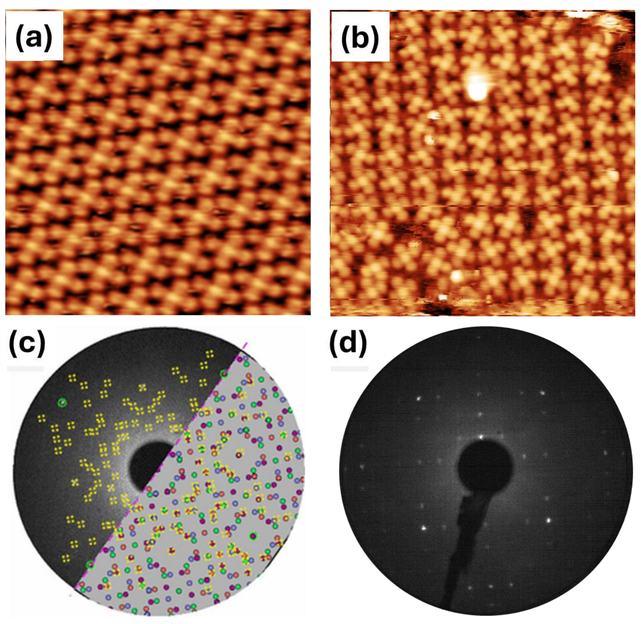


Figure 1: (a) STM image of high density structure of RuPc on Ag (100), 12x12 nm, -2 V tip bias, (b) the novel 6x6 structure of RuPc on Ag(100), 30x30 nm, -2 V tip bias (c) LEED pattern for high density RuPc[1] and (d) LEED of 6x6 reconstruction of RuPc on Ag (100)

MgO deposition on Ag (100)

MgO thin film was deposited on Ag (100) using a well-established reactive oxidation method[2]. Less than 1 ML of MgO forms islands of approximately 50 nm on Ag surface as shown in (a). STS confirmed the presence of clean patches of Ag between MgO islands indicating that the Ag surface is not completely covered by MgO. Increasing the deposition to 1.3 ML an almost continuous MgO layer is obtained (b). Due to the interesting property of maintaining a band gap compatible to the bulk one even in thin films, MgO was chosen as a decoupling layer between RuPc molecules and Ag (100).

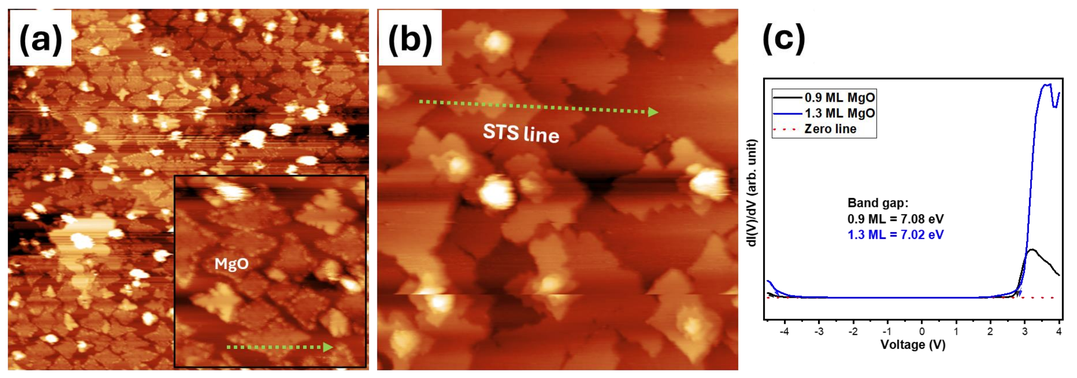


Figure 2: (a) 0.9 ML of MgO deposited on Ag (100), 500x500 nm, +4V gap voltage. The inset shows a zoom in of 100x100nm (b) 1.3 ML MgO deposition on Ag (100), 150x150 nm, +4V gap voltage. (c) STS obtained by averaging 20 measurements collected along the lines reported in Figure (a) and (b) (green arrows). The spectra exhibit a wide band gap compatible with the bulk MgO.

RuPc @ MgO/Ag(100)

Deposition of 1ML of RuPc at room temperature on the prepared MgO/Ag(100) results in formation of less order layer of RuPc as shown in Figure 3 (a). Applying positive bias to the tip images the lowest unoccupied molecular orbitals (LUMO), Figure 3(b) whereas negative tip bias shows the highest occupied molecular orbitals (HOMO). Since the molecules are not ordered therefore, it was not possible to obtain a clean STS.

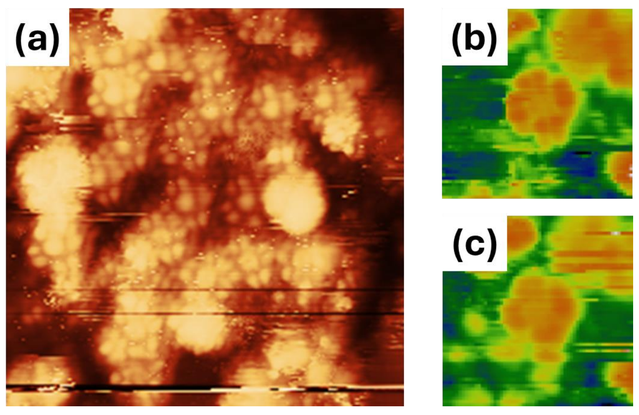


Figure 3: STM image of less ordered RuPc at MgO/Ag(100), 30x30 nm, 1.5 V gap voltage. LUMO and HOMO shape of RuPc molecules on MgO/Ag observed at tip bias +2V (b) and -2V (c) respectively.

Single RuPc on MgO/Ag(100)

Annealing at a moderate temperature 1 ML RuPc layer on MgO/Ag(100) causes desorption of RuPc molecules which makes it possible to observe single RuPc molecule (a) sitting on top of MgO islands (c) grown over Ag(100). STS of these single molecules have shown a shift from 0.72 V to 0.93 V when compared with STS of RuPc on clean Ag (100). This significant shift in the STS peak is related to the role of MgO decoupler layer between Ag and RuPc and has affected the electronic properties of RuPc molecules. Details of this effect are under further investigation.

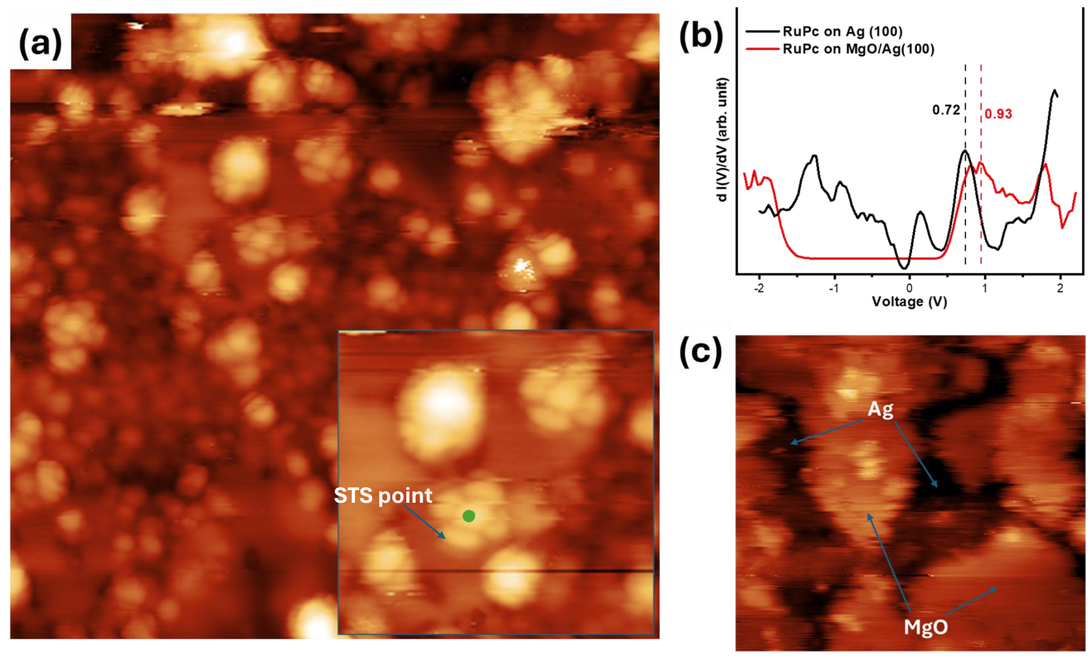


Figure 4: (a) STM image of RuPc molecules on MgO/Ag(100) after annealing, 30x30nm, -2V gap voltage. The inset shows zoom in on single RuPc molecuels and the green dot represents the point of STS. Comparison of STS of RuPc on Ag and RuPc on MgO/Ag is shown in (b). By changing the parameters of STM, we were able to image the MgO islands under the RuPc molecules confirming that the molecules are residing on MgO.

Conclusion

- MgO thin film shows a wide band gap even at one atomic layer thickness.
- More then 1 ML of RuPc molecules produce 6x6 reconstruction on clean Ag(100).
- RuPc molecules deposited on MgO/Ag(100) forms less ordered layer as compared to RuPc over clean Ag(100).
- STM shows that annealing the RuPc/MgO/Ag(100) produces a better surface and it is possible to observe single RuPc molecules over MgO islands.
- STS studies have depicted the shift in molecular orbitals of RuPc on MgO/Ag(100) as compared to RuPc/Ag(100).
- Shift in STS peak is related to the role of MgO as an electronic decoupler layer. Details of this effect are under further investigation.

Acknowledgment

We acknowledge the financial support of "ROME TECHNOPOLE a valere sul PNRR MISSIONE 4 – COMPONENTE 2 - INVESTIMENTO 1.5. Spoke 06-FP 05, cup-[B83C22002890005]

Reference

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