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Large-area α-MoO_3 Thin Films via Pulsed Laser Deposition for Polariton-Enhanced Infrared Molecular Sensing

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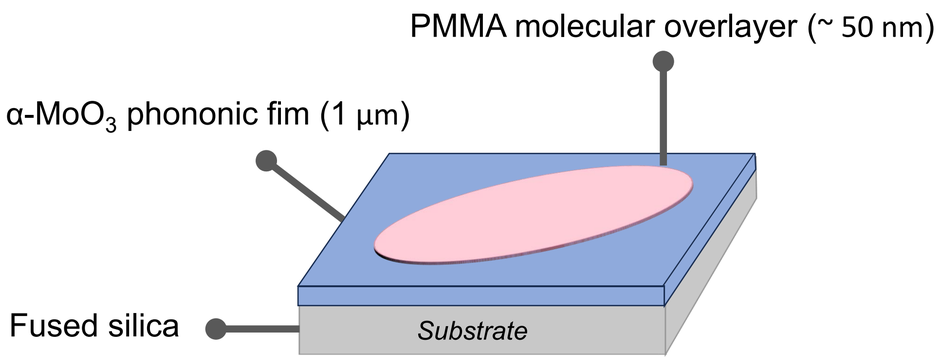
INTRODUCTION

Mid-infrared (mid-IR) spectroscopy provides direct access to the characteristic vibrational fingerprints of molecules, making it a powerful tool for chemical identification and molecular sensing. However, the intrinsically weak interaction between infrared radiation and ultrathin molecular layers often limits detection sensitivity. Surface-enhanced infrared absorption (SEIRA) approaches can overcome this limitation by enhancing the local electromagnetic field, although conventional platforms typically rely on lithographically engineered resonant structures [1]. Natural hyperbolic materials supporting phonon polaritons offer an attractive low-loss alternative, providing intrinsic optical resonances in the molecular fingerprint region. Among them, α-MoO_3 exhibits strongly anisotropic lattice vibrations and multiple Reststrahlen bands (RBs) across the mid-IR [2]. Here, we investigate large-area α-MoO_3 thin films grown by pulsed laser deposition (PLD) as scalable, lithography-free phononic platforms for infrared molecular sensing, using a thin PMMA overlayer as a model molecular system.

EXPERIMENTAL SETUP

Schematic illustration of samples under study



Experimental workflow

1 → 2 → 3

PLD-grown α-MoO_3

T(dep) = 450°C
$p(O_2)$ = 0.1 mbar
Substrate: quartz

PMMA deposition

PMMA = 0.1% (m/v), DCM
Drop-cast = 2 μL
Same deposition prvolumeotocol on Au and SiO_2 controls

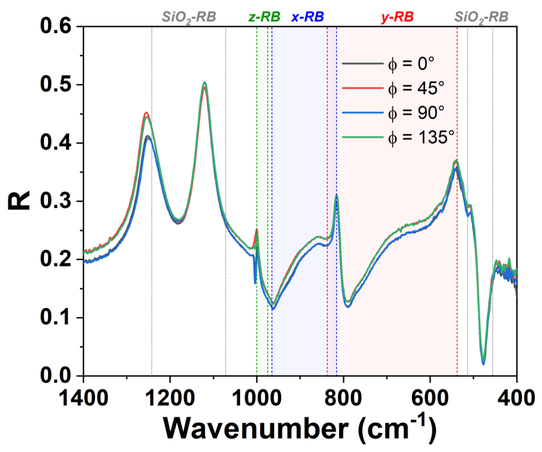
Micro-FTIR characterization

Bare and PMMA-coated regions measured locally on the same sample.

Mid-IR reflection measurements were performed using a Bruker INVENIO-R FTIR spectrometer coupled to a HYPERION II microscope, equipped with a thermoelectrically cooled mercury cadmium telluride (TE-MCT) detector. Regions with and without the PMMA coating were selected using the integrated video camera and subsequently characterized in near-normal reflection geometry using a 15× reflective objective (NA = 0.40). Spectra were acquired over the 6000–600 cm^{-1} range using a KBr beam splitter.

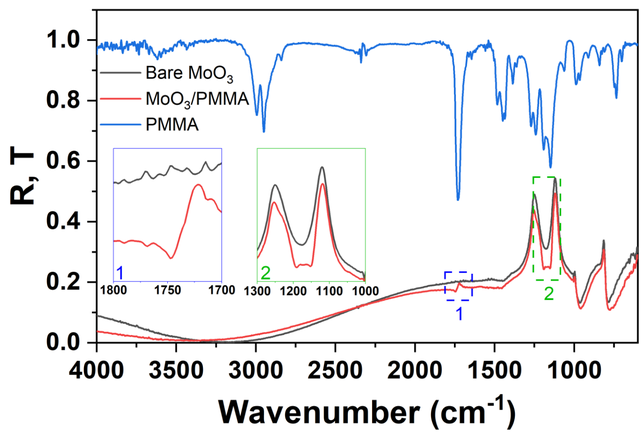
RESULT AND DISCUSSIONS

1. Intrinsic phonon resonances of α-MoO_3



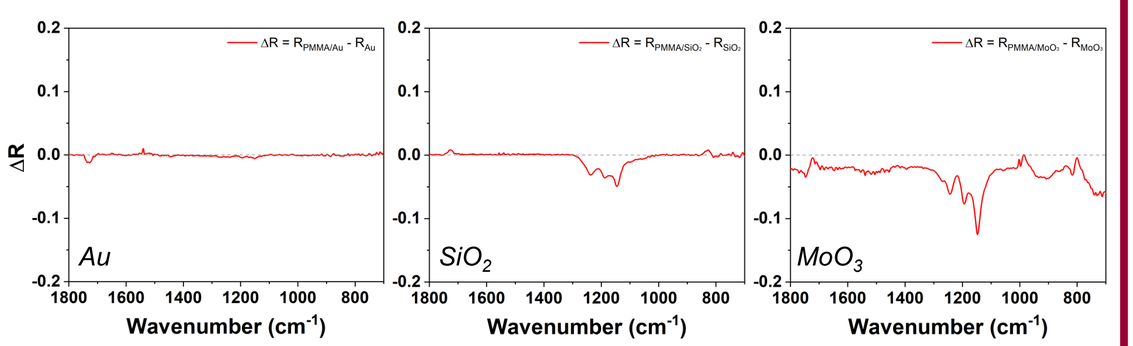
Multiple α-MoO_3 RBs provide structured phononic resonances across the MIR fingerprint region.

2. Molecular sensing



PMMA perturbs the α-MoO_3 reflectance response

3. Substrate-dependent molecular spectral response



The molecular spectral response is strongly substrate-dependent, with α-MoO_3 providing the largest reflectance modulation.

Conclusion. Large-area PLD-grown α-MoO3 thin films exhibit multiple intrinsic phonon resonances across the mid-IR fingerprint region. The deposition of a thin PMMA overlayer (~50 nm) produces distinct modifications of the reflectance response at characteristic molecular vibrational frequencies. Comparison with reference substrates reveals a substrate-dependent response, with α-MoO3 providing the strongest molecular spectral contrast. These results indicate that the intrinsic phonon resonances of α-MoO3 can be exploited to enhance molecular spectral contrast without the need for engineered resonators, providing a scalable and lithography-free platform for mid-IR molecular sensing.

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