Thin Solid Films 645 (2018) 215–221

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Single-crystalline silver films on mica

Dah-An Luh[a,b,*], Chen-Wei Liu[a], Cheng-Maw Cheng[b], Ku-Ding Tsuei[b], Chia-Hsin Wang[b], Yaw-Wen Yang[b]

[a] Department of Physics, National Central University, Taoyuan 32001, Taiwan
[b] National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan

ARTICLE INFO

Keywords:
Ag film
Mica
Ag(111) single crystal

ABSTRACT

Highly ordered Ag films grown on cleaved mica with a two-step procedure were characterized in detail with several techniques for surface analysis, including low-energy electron diffraction, X-ray photoemission spectra, a scanning tunneling microscope and angle-resolved photoemission spectra. Silver films of a thickness ≥ 100 nm were deposited on mica substrates at 300 K and stored under ambient conditions. The Ag/mica films became atomically flat and free of contamination when they were transferred into ultra-high vacuum and prepared with sputtering and annealing. The experimental results indicate that the surfaces of the cleaned Ag/mica films have structural and electronic properties resembling those of a Ag(111) single crystal with ordered domains aligned over a macroscopic region, but the surfaces of the Ag/mica films became rough on annealing above 623 K. On the rough surfaces, the surface steps tended to bunch together, yielding flat terraces bound with steps of large heights. With the decreased thermal stability in mind, the Ag/mica film is adoptable as a cheap platform alternative to a Ag(111) single crystal for the growth of highly ordered overlayers.

1. Introduction

The surfaces of single crystals constantly attract great interest because of their roles in both fundamental research on surface science and industrial applications. The highly ordered surfaces of single crystals on a macroscopic scale simplify greatly the analyses of the complicated physical and chemical properties of surfaces. Moreover, the surfaces of single crystals serve as well-defined platforms on which to construct highly ordered heteroepitaxial overlayers and nanostructures that might possess novel properties. The importance of the surfaces of single crystals increased because exotic two-dimensional (2D) materials have been recently developed. For example, graphene grown on polycrystalline metallic foils unavoidably consists of misaligned domains, resulting in a quality less than that obtained through mechanical exfoliation [1]. To resolve this issue, researchers have attempted to grow graphene on the surfaces of metallic single crystals [2–5]. The surfaces of metallic single crystals were also adopted to grow novel 2D materials, such as silicene on Ag(111) [6,7], MoS_2 on Au(111) [8], germanene on Au(111) [9] and Al(111) [10] and self-assembled monolayers (SAMs) on Au(111) [11]. Despite their great potential in the growth and applications of 2D materials, utilizing metallic single crystals has drawbacks. First, metallic single crystals are too expensive to be disposable like polycrystalline metallic foils. Second, they are conducting, making problematic the construction of electronic devices from overlayers grown thereon. To address these issues, some researchers substituted metallic single crystals with metallic films grown on highly ordered insulating substrates. After the overlayers of high quality are grown, the metallic films can be etched away; the overlayers can be transferred to other substrates or left on the insulating substrates for further processes [12–15].

Several insulating substrates, such as muscovite mica, sapphire and MgO, have been adopted to grow highly ordered metallic films. Muscovite mica is prominent among them because of its unique property such that it belongs to the group of phyllosilicates that can be cleaved easily to yield large atomically flat surfaces. Previous authors reported that Ag films on mica can be highly ordered; their surfaces appear to be Ag(111), and their surface morphology depends on both the rate of deposition of Ag and the temperature of the mica substrate [16–19]. The Ag films seem flatter at a greater rate of deposition of Ag and with a growth temperature 490–623 K, although they become rough at higher growth temperatures. In addition, there exist deep holes through the ordered Ag/mica films [17,18]. Although these authors suggested the possibility to adopt the metallic films on mica as cheap substrates alternative to metallic single crystals, detailed comparisons among them have yet to be made. In this work, we characterized the Ag films on mica grown with a two-step procedure different from the previous methods; in this procedure, Ag was deposited at 300 K and then annealed at a desired temperature. The samples were

* Corresponding author at: Department of Physics, National Central University, Taoyuan 32001, Taiwan.
E-mail address: luh.dah.an@gmail.com (D.-A. Luh).

http://dx.doi.org/10.1016/j.tsf.2017.10.051
Received 11 August 2017; Received in revised form 22 October 2017; Accepted 27 October 2017
Available online 28 October 2017
0040-6090/

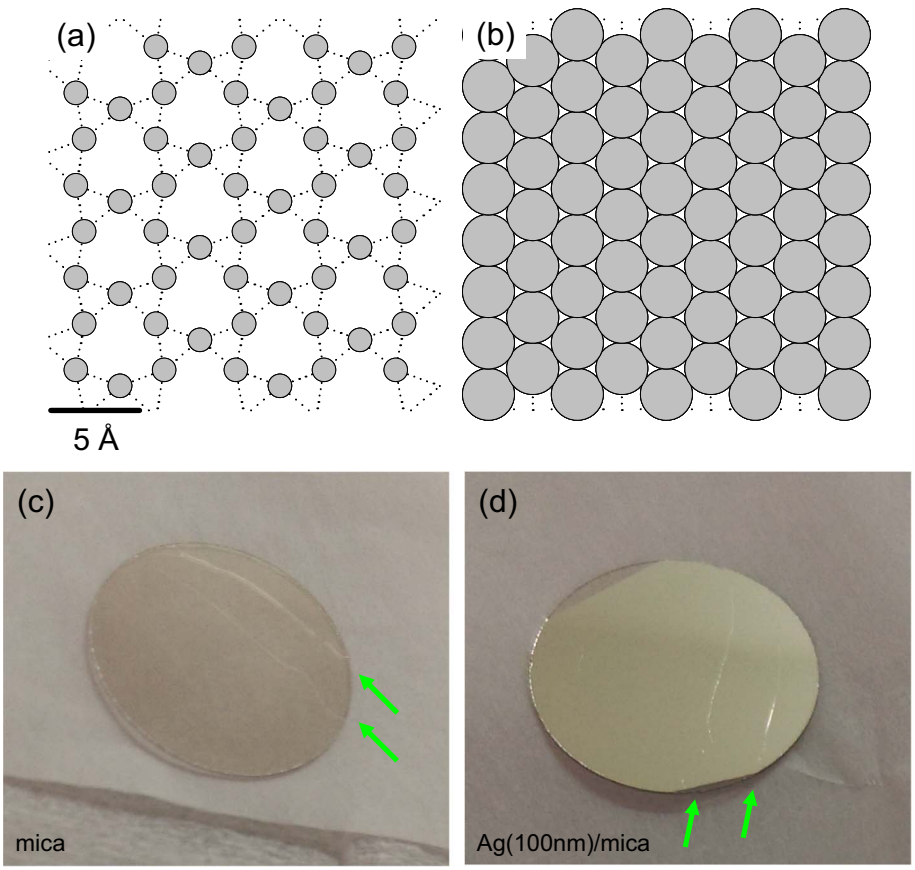

Fig. 1. (Color online) Sketches of surface structures of (a) cleaved mica (b) Ag(111). Only a network of O atoms is shown in (a). The covalent radii of O (0.66 Å) and Ag (1.45 Å) were used to draw the sketches. Photographs of a mica disk (diameter 10 mm) (c) just cleaved and (d) covered with Ag(100 nm). The green arrows indicate the surface steps. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

analyzed with techniques of surface analysis, including low-energy electron diffraction (LEED), X-ray photoemission spectra (XPS), a scanning tunneling microscope (STM) and angle-resolved photoemission spectra (ARPES). Our results show that the surfaces of the Ag films grown *ex situ* on mica became free of contamination and highly ordered with sputtering and annealing; the entire surfaces appear to be Ag(111) without misaligned domains. These Ag/mica films seem, however, less thermally stable than Ag(111) single crystals; their surfaces become rough when annealed above 623 K. Our results indicate that, with decreased thermal stability in mind, the Ag films on mica can serve as a cheap alternative to a Ag(111) single crystal, opening the possibility to grow overlayers of exotic 2D materials of high quality for mass production.

2. Experimental details

Commercially available disks of muscovite mica (diameter 10 mm, thickness 0.21 mm) served as substrates. Silver was deposited on cleaved mica at 300 K in an e-beam evaporation system with base pressure 1×10^{-7} Torr; the rate of deposition, monitored with a quartz crystal microbalance, was ~2 Å/s. The mica disks were cleaved under ambient conditions and then installed in the evaporation system; they did not undergo any cleaning procedure in vacuum before Ag was deposited. After deposition, the samples were removed from the evaporation system and stored in plastic boxes under ambient conditions. Because the evaporation system was not equipped with tools for surface analysis, the Ag films were not characterized before exposed to air. To obtain clean and ordered surfaces, we transferred the thin-film samples into ultra-high-vacuum (UHV) systems and treated them with cycles of ion sputtering (Ar 3×10^{-5} Torr, high-voltage bias 1 kV) and annealing. During annealing, the sample temperature was increased slowly to the desired temperature and retained there for 5 min. Our experiments indicated that the duration for which the Ag/mica samples were stored under ambient conditions did not affect the experimental results.

The LEED and XPS measurements were performed at an end station installed at Taiwan Light Source beamline BL24A1 of National Synchrotron Radiation Research Center (NSRRC). Because mica is insulating, the Ag films were grounded with pieces of Mo foil pressed onto the film surfaces during measurements. XPS were recorded with an electron energy analyzer (SPECS PHOIBOS 150). With the grating of the beamline employed in this study, the photon energy was variable from 120 to 350 eV, mixed with high-order harmonics in substantial proportion. The beamline was set at 340 eV for XPS measurements; the core levels were excited with photons of energy ~340 eV and ~680 eV simultaneously. With the setup, the core levels of interest in this work, such as C 1s, O 1s, Si 2p, S 2p and Ag 3d, were accessible in a single measurement. The ARPES were recorded at an end station installed at beamline BL21B1 of NSRRC. The angle-resolved energy distributions were recorded with an electron energy analyzer (Scienta R4000) with angular resolution better than 0.1°. The sample was installed on a 6-axis manipulator. The axis of the acceptance cone of the analyzer and the incident direction of the photon beam were fixed at angle 45° to each other; the sample was rotated to explore the electronic structure in the desired reciprocal space. The STM measurements were performed on a variable-temperature STM (RHK UHV 300) in a separate UHV system; chemically etched W wires served as tips. The sample temperature was determined with a thermocouple junction pressed onto the film surface; the same thermocouple junction served to bias the Ag film during measurements. To deposit Bi onto the Ag/mica surface, we evaporated Bi with an e-beam evaporator (Omicron EFM3); the sample was then characterized *in situ*.