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Muscovite mica: Flatter than a pancake

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ABSTRACT

Muscovite mica is a widely used material because of its transparency, heat resistance and especially its flatness. This study investigates how flat muscovite mica really is. The surface of cleaved muscovite mica was studied with the help of several optical techniques, surface X-ray diffraction and with atomic force microscopy. The results show that for high-quality muscovite mica, large (>1 cm^2) step-free surface areas exist, which makes it one of the flattest materials around. Several reasons are given to explain why this crystal is so incredibly flat. The flatness of muscovite mica can be exploited in applications such as the surface force apparatus and creating a flat interface for organic solar cells.

1. Introduction

Muscovite mica was used in X-ray diffraction as early as 1912 by W.L. Bragg to examine whether X-rays are very short electromagnetic waves, as was suggested by Max v. Laue [1]. W.L. Bragg suggested that these waves should be regularly reflected by a sufficiently flat surface, hence muscovite mica was chosen. His experiment showed that the X-ray beam was diffracted by the bulk crystal rather than reflected by the surface. The structure of muscovite mica was first studied in 1927 by Maugain using X-ray diffraction [2]. More recently, muscovite mica has become a possible template in the hypothesis of a surface-mediated origin of life [3,4]. The high affinity of the muscovite mica surface for DNA, oligonucleotides and lipids makes such a hypothesis plausible [5–8]. In geology muscovite mica is used to map hydrothermal mineralization systems [9] and also as a means to determine the age of rocks via $^{40}Ar/^{39}Ar$ dating, in order to investigate geological and tectonic history [10]. Furthermore, muscovite mica has commonly been used in furnace windows because of its heat resistance and transparent properties. Mica can even be found in some shower gels, to add lustre and colour [11].

A sample of (001) muscovite mica (monoclinic, $a = 0.51906$ nm, $b = 0.9008$ nm, $c = 2.0047$ nm, $\beta = 95.757°$, space group $C\,2/c$, chemical formula $KAl_2(Si_3Al)O_{10}(OH)_2$) is easy to cleave along the *ab*-plane, giving a clean and flat surface. Because the surface is atomically flat, muscovite mica is a suitable substrate material for the self-assembly of molecular layers [12–15] and the study of thin films, for example of Pt [16]. Because of its flatness, muscovite mica has also been used as a substrate for the imaging of graphene. The muscovite mica substrate proved to be several times better than a SiO_2 substrate in terms of the observed graphene roughness [17,18].

A special application of muscovite mica can be found in the surface force apparatus (SFA) where it is used because of its transparency and especially its flatness [19,20]. In a different application, muscovite mica is used as a template to produce the active layer for organic solar cells. The interface of the active layer will be extremely flat as a result of using muscovite mica, thus creating a better contact with the other layers and a better device [21].

It is possible to modify the mica surface for protein crystallisation purposes [22,23] and surface ions can be exchanged for a variety of alkali metal ions [24,25]. Changing the surface ions has a direct effect on the ordering of the water layers, which is called structure breaking or promoting [5,19]. Besides the SFA, surface X-ray diffraction (SXRD), atomic force microscopy (AFM), molecular dynamics simulations and X-ray reflectivity have also been used to determine the surface structure of modified mica and its liquid surface layer [25–32].

Because of its glide plane along the *c*-axis, the (001) surface of muscovite mica can have two different terminations, which are mirrored with respect to each other in the (010) plane (shown in Fig. 1). The different surface terminations on the mica surface are separated by steps of ½ $\vec{c}$, or 1.002 nm, in height.

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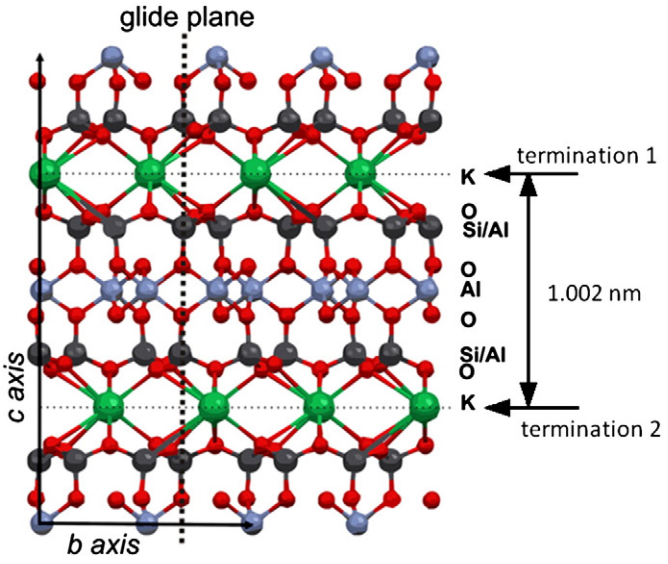

Fig. 1. Ball and stick model of muscovite mica, showing a glide plane along the *c*-axis (dashed vertical line).

It has been shown that the different terminations can be observed through polarised fluorescence microscopy, if a layer of para-hexaphenylene is grown on to the muscovite mica. The para-hexaphenylene grows epitaxially along the [110] direction of the muscovite mica crystal and this direction is shifted by 60° when a change in termination occurs. This change in termination is easy to observe with polarisation microscopy. Therefore, this technique is very suitable for the detection of steps with an uneven number ($2n+1$ nm), but it is more difficult to distinguish steps of an even number ($2n$ nm) [15].

Muscovite mica is widely used because of its flatness, but to the best of our knowledge it has not been investigated how flat muscovite mica is over large areas (more than (200×200) μm^2). Therefore, this study aims to investigate how flat muscovite mica is over larger distances and to explain why this happens. To achieve this, the surface of high- and low-quality muscovite mica was investigated with the help of phase contrast microscopy, atomic force microscopy, phase shifting interferometry and surface X-ray diffraction. High-quality muscovite mica can be visually distinguished from low-quality muscovite mica by the absence of incorporated (yellow) contaminants.

2. Experimental

2.1. Specimen preparation

High-quality muscovite mica of 0.3 mm in thickness (quality grade ASTM-V-1) was obtained from S&J Trading Inc., Glen Oaks NY, USA; and low-quality (quality grade ASTM-V-1/V-2) mica was purchased from Dumico, Capelle aan de IJssel, The Netherlands. The definition for these qualities is as follows: "V-1: Clear — Hard, of uniform colour, nearly flat, free of all stains, foreign inclusions, cracks, and other, similar, defects. V-2: Clear and Slightly Stained — Hard, of uniform colour, nearly flat and may contain slight discoloration, and very slight air inclusions and not more than in one fourth of the usable area" [33].

An atomically flat surface of 1 mm^2 can be obtained by using simple adhesive tape to cleave the muscovite mica. However, this was improved by cleaving a 0.3 mm thick substrate down the middle. A sharp knife was used to make an incision and the two crystal halves were pulled apart manually. During the cleaving it was found to be extremely important to bend the crystal as little as possible, in order to reduce stress on the crystal during cleaving and obtain a flat surface.

For phase contrast microscopy experiments, a 15 nm silver layer was evaporated on top of the muscovite mica surface using an in-house built e-beam evaporator.

Potassium acid phthalate (KAP) (Reag. Ph Eur) was obtained from Merck. KAP crystals were grown from water solutions (ultrapure, 18.2 MΩ/cm resistance and <3 ppb organic content) to serve as a reference sample with known step height. This was done in order to show that the microscope was sensitive enough to detect steps of 1 nm. A droplet of a saturated aqueous KAP solution was placed on a microscope glass slide and left to evaporate, so crystallisation could occur. After approximately 5 min of evaporation, the remaining water was blown off using an intense nitrogen flow. This resulted in a clean KAP crystal surface as was also reported in [34,35]. A silver layer was applied to the KAP surface in a similar way as for the muscovite mica.

2.2. Optical surface characterization

Step heights were determined with the help of several different techniques. AFM (Dimension 3100) was applied in intermittent contact mode with NSG 10 golden silicon probes from NT-MDT. Steps can easily be revealed by AFM; however, this method is not ideally suited for the examination of surface areas larger than (100×100) μm^2. Optical phase sensitive microscopy is more advantageous to uncover steps on larger surface areas if the steps are separated by a distance larger than the wavelength of the yellow light used (580–600 nm). Phase contrast microscopy and phase shifting interferometry (PSI) are capable of detecting height differences of less than 1 nm [36–39]. In this study these techniques are used to scrutinise the mica surface for ½ $\vec{c}$ and higher steps, to validate the occurrence of large areas with single termination. An optical surface profiler (Veeco WYKO NT1100) was used in PSI mode to analyse the surface morphology. Finally, an optical reflection phase contrast microscope (Reichert MeF2), fitted with a high absorption phase plate (95%), was used to explore large mica surface areas for the occurrence of steps.

2.3. Surface X-ray diffraction

SXRD was used to identify and to determine the extent of the two different terminations on the muscovite mica surface by measuring surface sensitive diffraction rods [40]. SXRD was performed at beam line ID03 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, using a vertical z-axis diffractometer equipped with a 2D detector in the stationary geometry [41]. The momentum transfer in the X-ray diffraction experiments is denoted by $\vec{Q} = h \cdot \vec{a}^* + k \cdot \vec{b}^* + l \cdot \vec{c}^*$, with $\vec{a}^*$, $\vec{b}^*$ and $\vec{c}^*$ the reciprocal lattice vectors and (hkl) the diffraction indices. The diffraction rods are along the l-direction. Because of the (010) glide plane, the diffracted intensity along the (hk) rod from termination 1 is the same as that of the $\left(h\bar{k}\right)$ rod of termination 2 (see Fig. 1). The diffracted intensities on termination 1 of (hk) and $\left(h\bar{k}\right)$ are different. If over the measured surface area both terminations are equally present, the two rods will therefore be equal, but otherwise not.

Two types of experiments were performed. First, a full set of (11) and $\left(1\bar{1}\right)$ rods were measured in order to determine the surface termination and observe the presence of a single step. Secondly, using only the (111.4) and $\left(1\,\bar{1}\,1.4\right)$ reflections, an even larger area was determined to be step free.

The first measurement was performed using a 16 keV beam with 3 mm horizontal width, 30 μm vertical width and an incoming angle of 0.6°. This led to a footprint of 3 by 3 mm. A controlled humidity cell was used. Further details are described in [42].

In the second measurement, surface termination mapping, using the (111.4) and $\left(1\,\bar{1}\,1.4\right)$ surface reflections, was performed using a 15 keV