

## Effect of the surface texture at the interface on the friction induced crystal growth of 2D layered MoS<sub>2</sub>

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### Abstract

We used X-ray Diffraction (XRD) and Raman Spectroscopy to demonstrate the formation of atomic layers of MoS<sub>2</sub> using a novel friction induced crystal growth method. The MoS<sub>2</sub> crystal was grown by friction at the interface between stainless steel and high carbon chromium bearing steel (SUJ2). The MoS<sub>2</sub> was produced mechanochemically from molybdenum dialkyl dithiocarbamate (MoDTC) mixed with synthetic oil. The friction experiments were carried out with a load of 10 N at a sliding speed of 2.5 mm/sec in an oil-bath at a temperature of 80°C. We investigated the effect of the surface conditions of the stainless steel substrates on the formation of the MoS<sub>2</sub>. The parameters examined were the surface composition, the hardness and the roughness of the substrates. Crystalline MoS<sub>2</sub> was formed on the stainless steel surfaces with higher Cr composition and lower hardness. Furthermore, the quality of the MoS<sub>2</sub> crystal improved when the substrate had less surface roughness. The results indicate that the crystal growth of MoS<sub>2</sub> can be optimized by the choice of substrate, particular with regard to the Cr content and the surface roughness, and the friction conditions.

**Keywords** Two-dimensional material; Molybdenum disulfide; Friction induced crystal growth stainless steel; Hardness; Roughness

### Introduction

Because the physical and chemical properties of 2D materials are different from their bulk counterparts, the interest in these materials has, in recent years, been on the increase [1]. The optoelectronic properties of two dimensional (2D) transition metal dichalcogenides (TMDC) make them promising materials for future devices [2,3]. Molybdenum disulfide is one type of TMDC.

Monolayers of MoS<sub>2</sub> semiconductor can be used for high speed, low power transistors [4,5], superconductors [6,7] and as highly active catalysts [8]. The bandgap of MoS<sub>2</sub> depends on the number of layers. As the number of layers decreases to a monolayer, the bandgap increases from 1.29 eV (indirect) to 1.8 eV (direct) as it approaches the 2D state [9,10]. MoS<sub>2</sub> having an ultrathin atomic layered structure is an interesting semiconductor material for a new generation of devices. Field effect transistors (FETs) with lower power consumption and higher frequency operation can be realized [4]. For these studies, the MoS<sub>2</sub> crystals were prepared by two methods. One was mechanical exfoliation [11,12], the other was chemical vapor deposition (CVD) [13-15]. On the other hand, layered MoS<sub>2</sub> has also been used as a lubricant [16]. This reduces friction at the interface between mechanical parts, where each layer slides easily under a small shear stress as a result of the weak van der Waals bonding force of the layered structure [17]. At the interface, MoS<sub>2</sub> is mechanochemically synthesized from molybdenum dialkyl dithiocarbamate (MoDTC) in synthetic oil [18]. A low friction interface is realized in well-stacked layered MoS<sub>2</sub>. This reduction reaction is used to reduce piston ring friction in car engines. We previously proposed a novel method in which the friction is used to induce the growth of 2D layered MoS<sub>2</sub> crystals [19]. In our previous study, we measured the XRD diffraction,

Raman and photoluminescence (PL) spectra of MoS<sub>2</sub> crystals grown at the interface between SUS430 stainless steel and high carbon chromium bearing steel (SUJ2). The structure of the MoS<sub>2</sub> was layered with the c-axis perpendicular to the surface. The thickness was N-layers (N>6). The PL peak of the neutral exciton emission was observed at RT, which suggests that the crystalline quality was good with low impurities and defects [20]. Such MoS<sub>2</sub> crystals can be used for fabricating semiconductor devices. In this study, the effect of the surface composition, the hardness and the roughness of the stainless steel substrate on the friction induced crystal growth of 2D layered MoS<sub>2</sub> was investigated in order to explore the conditions needed to improve the crystalline quality as well as enlarge the size of the crystals.

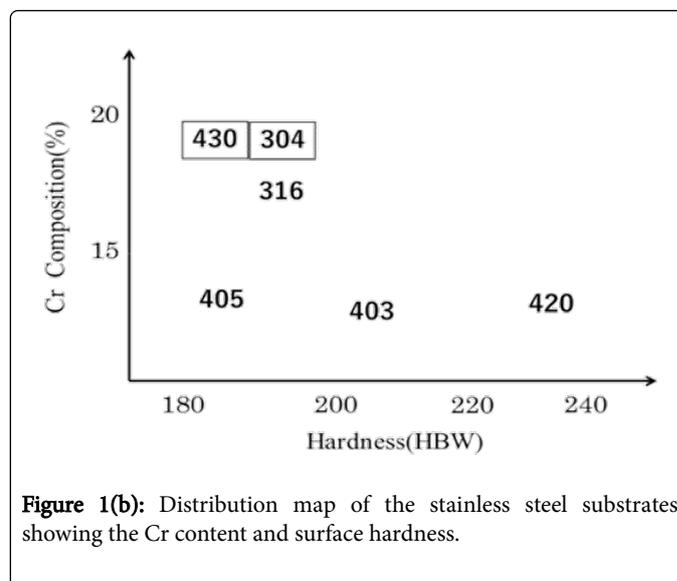
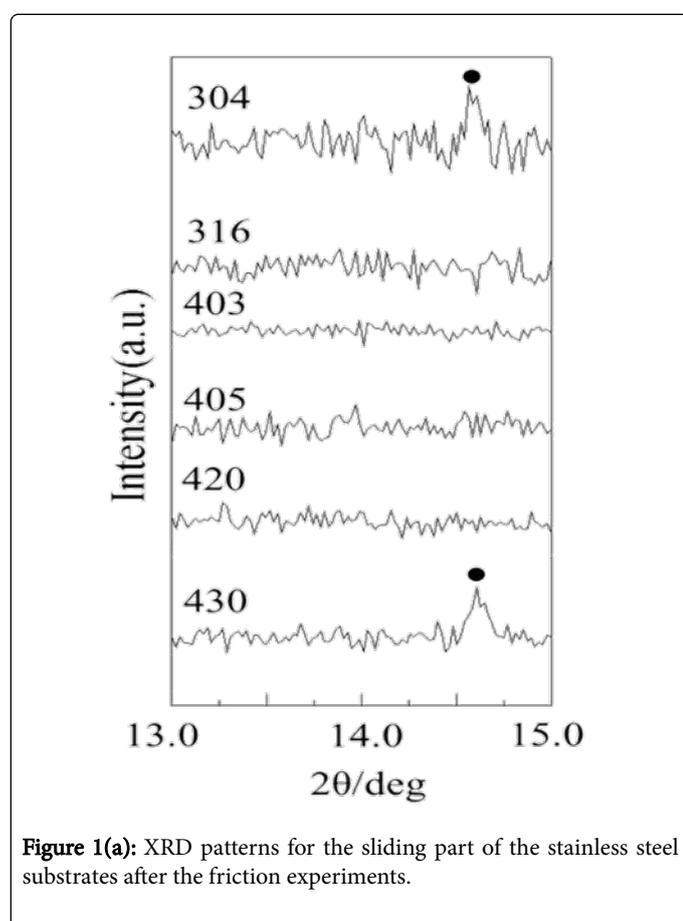
### Materials and Methods

The friction induced crystal growth was conducted using a ball on plate method on a rotating stage. The details have been described in one of our previous studies [19]. Six different stainless steel substrates were examined: SUS304, SUS316, SUS403, SUS405, SUS420 and SUS430. The surface of each substrate was mechanically polished by #400 paper. For SUS430, two substrates were prepared with different RMS surface roughnesses of 0.02 μm and 0.002 μm by ultra-precise polishing (TDC Corporation). The ball was 8 mm in diameter and made of high carbon chromium bearing steel (SUJ2), and had a surface roughness of 0.008 μm. These roughnesses were measured using a 3D laser microscope (Shimadzu OLS4100). The friction experiments were performed under a load of 10 N with a sliding speed of 2.5 mm/s for 30 min. A synthetic oil, poly-α-olefin (PAO), at a temperature of 80°C was used in the experiments. This was blended with the molybdenum dithiocarbamate (MoDTC) and calcium sulfonate. For each stainless steel substrate, the formation of MoS<sub>2</sub> was analyzed using X-ray diffraction measurements (Bruker D8 Advance) with Cu Kα radiation (λ=0.154 nm). For the SUS430 substrates, room-temperature μ-Raman spectra were measured in the back-scattering configuration using a

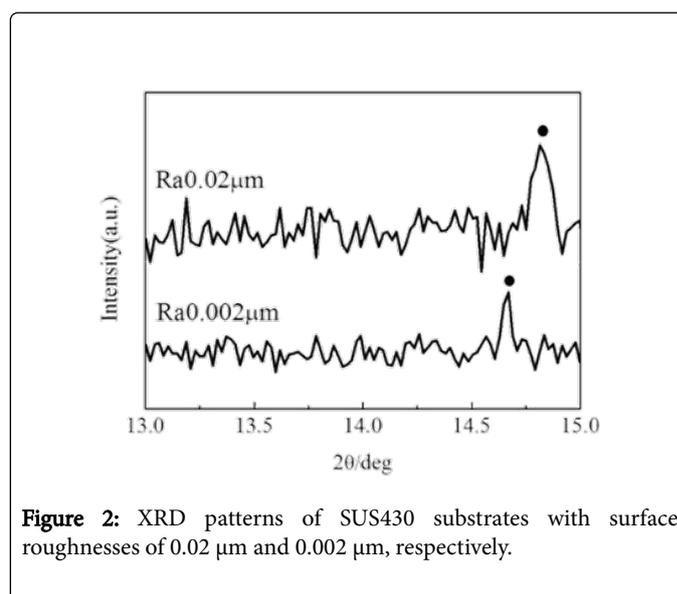
JASCO NRS-5100 spectrometer after rinsing the substrates in alcohol. Excitation was by a 0.8 mW SHG YVO4 laser operating at 532 nm. The laser was focused onto the substrate by a 100×objective lens. The beam spot size was about 1 μm in diameter, which is close to the diffraction limit defined by the laser wavelength. The spectral resolution was 0.4 cm<sup>-1</sup>.

## Results and Discussion

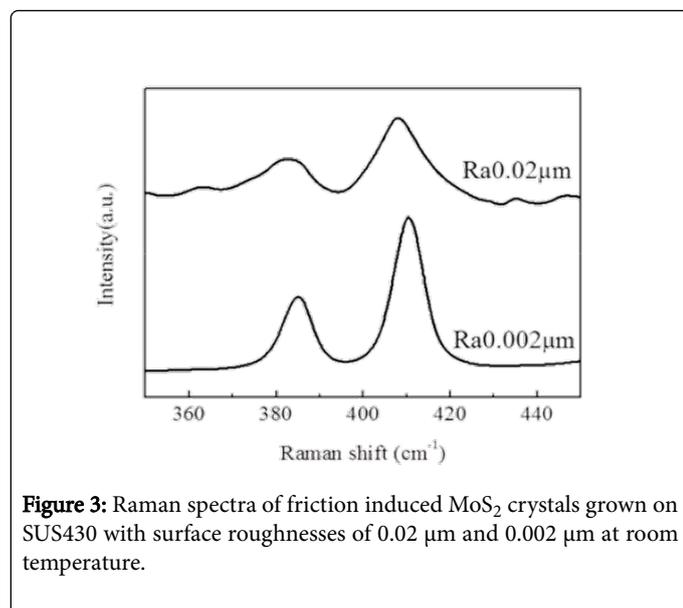
Figure 1(a) shows XRD patterns for the sliding parts of the stainless steel substrates after the friction experiments. A diffraction peak at 2θ=14.6° appears for the SUS304 and SUS430 substrates, which corresponds to the (002) plane of hexagonal MoS<sub>2</sub> (JCPDS card No: 75-1539), indicating that crystalline MoS<sub>2</sub> has been formed on these substrates. A distribution map of the Cr content and surface hardness of the substrates is plotted in Figure 1(b).



The materials on which MoS<sub>2</sub> is most easily formed, SUS304 and SUS430, have higher Cr content and lower surface hardness than the other types of steel. It is thought that chromium acts as a reductant to enhance the formation of MoS<sub>2</sub> from MoDTC. The lower hardness of the SUS430 and SUS304 substrates means the gap between the two metal surfaces is very narrow which enhances the formation of MoS<sub>2</sub> due to the dynamic change in pressure and temperature of the MoDTC in PAO. This reduction reaction mechanism of MoDTC to MoS<sub>2</sub> is discussed below. The XRD patterns of SUS430 substrates with surface roughnesses of 0.02 μm and 0.002 μm are shown in Figure 2.



The diffraction peak for MoS<sub>2</sub> with Ra=0.02 μm is broader and located at a higher angle than that for MoS<sub>2</sub> with Ra=0.002 μm. The inter-planar spaces between the layers of MoS<sub>2</sub> grown on SUS430 with surface roughnesses of 0.02 and 0.002 μm were calculated to be 5.99 Å and 6.03 Å, respectively, using Bragg's equation. The difference is due to the larger compressive strain in the MoS<sub>2</sub> crystal on the surface with Ra=0.02 μm arising from the smaller contact area and greater number of contact points with the SUJ2 ball.



**Figure 3:** Raman spectra of friction induced MoS<sub>2</sub> crystals grown on SUS430 with surface roughnesses of 0.02 μm and 0.002 μm at room temperature.

Figure 3 shows Raman spectra of friction induced MoS<sub>2</sub> crystals grown on SUS430 with surface roughnesses of 0.02 μm and 0.002 μm at room temperature, in which two Raman vibrational modes, E<sup>1</sup><sub>2g</sub> and A<sub>1g</sub>, appear around 383 cm<sup>-1</sup> and 410 cm<sup>-1</sup>, respectively. These modes are attributed to in-plane vibrations of molybdenum and sulfur atoms and out-of-plane vibrations of sulfur atoms, respectively [21-23]. The distance of 25 cm<sup>-1</sup> between these two Raman frequencies indicates that the thickness is N-layers (N>6) of MoS<sub>2</sub>. The full width at half maximum (FWHM) of the E<sup>1</sup><sub>2g</sub> peak is used as an indicator of the crystalline quality [24]. Both the E<sup>1</sup><sub>2g</sub> peak and the A<sub>1g</sub> peak for MoS<sub>2</sub> grown on SUS430 with Ra=0.02 μm are broader than the corresponding peaks for MoS<sub>2</sub> grown on SUS430 with Ra=0.002 μm. The results of the Raman spectra are in agreement with those from the XRD diffraction measurements. Even though MoS<sub>2</sub> lubricant is used extensively, the tribochemical reaction mechanism of MoDTC has not been well researched. This reduction reaction only occurs under friction conditions. The dynamics at the interfaces between the lubricant and the metal surfaces are complex. The friction at the interface raises the temperature, pressure and shearing force, and these rapid changes at the interface induce the reduction reaction of MoDTC.

According to Hertz's contact theory [25, 26], the area and pressure of the contact points are estimated to be φ 100 μm and ~1 GPa, respectively under these conditions. Although the oil-bath temperature is 80 °C in this experiment, it is thought that the temperature at the friction interface is more than a few hundred °C. This high pressure and temperature gives rise to the mechanochemical formation of MoS<sub>2</sub>. As shown in Figure 1(a) and 1(b), the Cr composition and surface hardness affect the formation of MoS<sub>2</sub> [27]. Chromium is not only a catalyst for the reductive reaction but is also a functional additive for decreasing the thermal conductivity. The greater the Cr content, the lower the thermal conductivity. Thus, it is possible that the temperature at the interface is higher for the SUS430 and SUS304 substrates, where the formation of MoS<sub>2</sub> occurs most easily. However, one needs to take into account the fact that the thermal conductivity is influenced by other elements such as the amount of Ni. To fully clarify this mechanism, further experiments are needed.

## Conclusion

The effects of the composition, hardness and roughness of the surfaces of stainless steel on the friction induced crystal growth of 2D layered MoS<sub>2</sub> were investigated. XRD measurements indicated that MoS<sub>2</sub> crystals grew on stainless steel substrates with high Cr content and low surface hardness. Then load in the experiments was 10 N, and the sliding speed and temperature in the oil-bath were 2.5 mm/sec and 80 °C, respectively. Smaller roughness improved the crystalline quality of the MoS<sub>2</sub> crystal, which was confirmed by XRD diffraction and Raman spectroscopy measurements. These results will prove useful for optimizing the friction conditions and the quality of MoS<sub>2</sub> crystals grown by the friction induced method on stainless steel surfaces.

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