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Research

# Surface Texture Effects on Friction-Induced Crystal Growth in 2D Layered $MoS_2$

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## Abstract

We used X-ray Diffraction (XRD) and Raman Spectroscopy to demonstrate the formation of atomic layers of $MoS_2$ using a novel friction induced crystal growth method. The $MoS_2$ crystal was grown by friction at the interface between stainless steel and high carbon chromium bearing steel (SUJ2). The $MoS_2$ 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 $MoS_2$. The parameters examined were the surface composition, the hardness and the roughness of the substrates. Crystalline $MoS_2$ was formed on the stainless steel surfaces with higher Cr composition and lower hardness. Furthermore, the quality of the $MoS_2$ crystal improved when the substrate had less surface roughness. The results indicate that the crystal growth of $MoS_2$ 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 di9erent from their bulk counterparts, the interest in these materials has, in recent years, been on the increase [1]. Ue 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 $MoS_2$ semiconductor can be used for high speed, low power transistors [4,5], superconductors [6,7] and as highly active catalysts [8]. Ue bandgap of $MoS_2$ 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]. $MoS_2$ having an ultrathin atomic layered structure is an interesting semiconductor material for a new generation of devices. Field e9ect transistors (FETs) with lower power consumption and higher frequency operation can be realized [4]. For these studies, the $MoS_2$ 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 $MoS_2$ has also been used as a lubricant [16]. Uis 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, $MoS_2$ is mechanochemically synthesized from molybdenum dialkyl dithiocarbamate (MoDTC) in synthetic oil [18]. A low friction interface is realized in well-stacked layered $MoS_2$. Uis 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 $MoS_2$ crystals [19]. In our previous study, we measured the XRD di9raction, Raman and photoluminescence (PL) spectra of $MoS_2$ crystals grown at the interface between SUS430 stainless steel and high carbon chromium bearing steel (SUJ2). Ue structure of the $MoS_2$ was layered with the c-axis perpendicular to the surface. Ue thickness was N-layers (N>6). Ue 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 $MoS_2$ crystals can be used for fabricating semiconductor devices. In this study, the e9ect of the surface composition, the hardness and the roughness of the stainless steel substrate on the friction induced crystal growth of 2D layered $MoS_2$ 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

Ue friction induced crystal growth was conducted using a ball on plate method on a rotating stage. Ue details have been described in one of our previous studies [19]. Six di9erent stainless steel substrates were examined: SUS304, SUS316, SUS403, SUS405, SUS420 and SUS430. Ue surface of each substrate was mechanically polished by #400 paper. For SUS430, two substrates were prepared with di9erent RMS surface roughnesses of 0.02 μm and 0.002 μm by ultra-precise polishing (TDC Corporation). Ue ball was 8 mm in diameter and made of high carbon chromium bearing steel (SUJ2), and had a surface roughness of 0.008 μm. Uese roughnesses were measured using a 3D laser microscope (Shimadzu OLS4100). Ue 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. Uis was blended with the molybdenum dithiocarbamate (MoDTC) and calcium sulfonate. For each stainless steel substrate, the formation of $MoS_2$ was analyzed using X-ray di9raction 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 aIer rinsing the substrates in alcohol. Excitation was by a 0.8 mW SHG YVO4 laser operating at 532 nm. Ue laser was focused onto the substrate by a 100×objective lens. Ue beam spot size was about 1 µm in diameter, which is close to the di9raction limit defined by the laser wavelength. Ue spectral resolution was 0.4 $cm^{-1}$.

## Results and Discussion

Figure 1(a) shows XRD patterns for the sliding parts of the stainless steel substrates aIer the friction experiments. A di9raction peak at $2\theta=14.6^{\circ}$ appears for the SUS304 and SUS430 substrates, which corresponds to the (002) plane of hexagonal $MoS_2$ (JCPDS card No: 75-1539), indicating that crystalline $MoS_2$ 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).

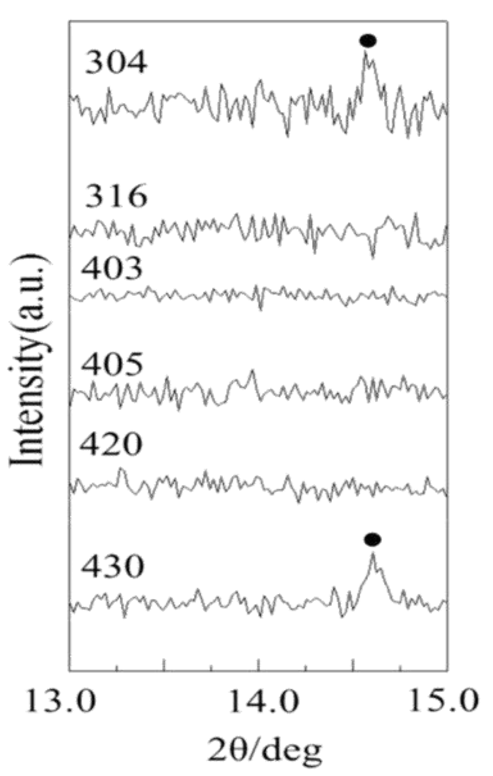


Figure 1(a): XRD patterns for the sliding part of the stainless steel substrates aIer the friction experiments.

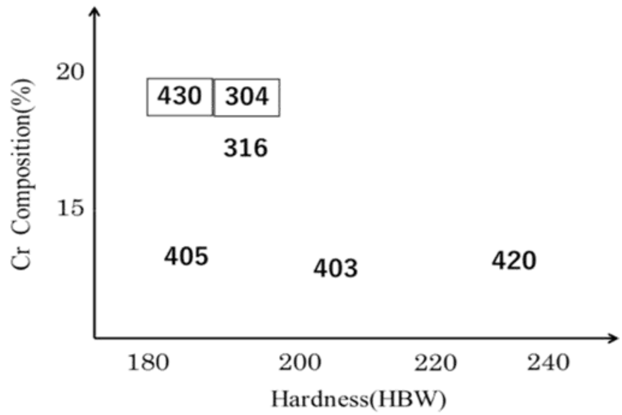


Figure 1(b): Distribution map of the stainless steel substrates showing the Cr content and surface hardness.

Ue materials on which $MoS_2$ 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 $MoS_2$ from MoDTC. Ue lower hardness of the SUS430 and SUS304 substrates means the gap between the two metal surfaces is very narrow which enhances the formation of $MoS_2$ due to the dynamic change in pressure and temperature of the MoDTC in PAO. Uis reduction reaction mechanism of MoDTC to $MoS_2$ is discussed below. Ue XRD patterns of SUS430 substrates with surface roughnesses of 0.02 µm and 0.002 µm are shown in Figure 2.

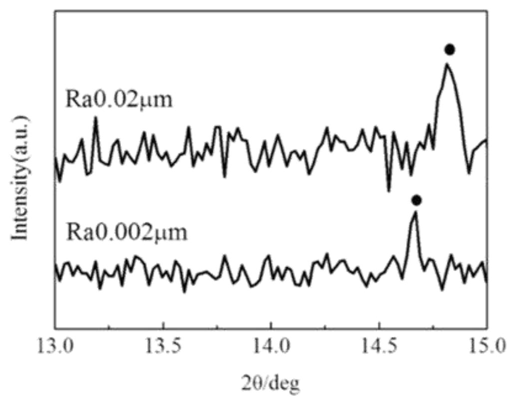


Figure 2: XRD patterns of SUS430 substrates with surface roughnesses of 0.02 µm and 0.002 µm, respectively.

Ue di9raction peak for $MoS_2$ with Ra=0.02 µm is broader and located at a higher angle than that for $MoS_2$ with Ra=0.002 µm. Ue inter-planar spaces between the layers of $MoS_2$ 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. Ue di9erence is due to the larger compressive strain in the $MoS_2$ 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.

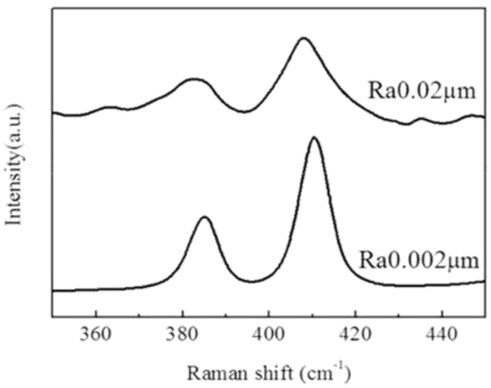


Figure 3: Raman spectra of friction induced $MoS_2$ crystals grown on SUS430 with surface roughnesses of 0.02 μm and 0.002 μm at room temperature.

Figure 3 shows Raman spectra of friction induced $MoS_2$ crystals grown on SUS430 with surface roughnesses of 0.02 μm and 0.002 μm at room temperature, in which two Raman vibrational modes, $E^1_{2g}$ and $A_{1g}$, appear around 383 $cm^{-1}$ and 410 $cm^{-1}$, respectively. Uese modes are attributed to in-plane vibrations of molybdenum and sulfur atoms and out-of-plane vibrations of sulfur atoms, respectively [21-23]. Ue distance of 25 $cm^{-1}$ between these two Raman frequencies indicates that the thickness is N-layers (N>6) of $MoS_2$. Ue full width at half maximum (FWHM) of the $E^1{}_{2g}$ peak is used as an indicator of the crystalline quality [24]. Both the $E^1_{2g}$ peak and the $A_{1g}$ peak for $MoS_2$ grown on SUS430 with Ra=0.02 μm are broader than the corresponding peaks for $MoS_2$ grown on SUS430 with Ra=0.002 μm. Ue results of the Raman spectra are in agreement with those from the XRD di9raction measurements. Even though $MoS_2$ lubricant is used extensively, the tribochemical reaction mechanism of MoDTC has not been well researched. Uis reduction reaction only occurs under friction conditions. Ue dynamics at the interfaces between the lubricant and the metal surfaces are complex. Ue 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. Uis high pressure and temperature gives rise to the mechanochemical formation of $MoS_2$. As shown in Figure 1(a) and 1(b), the Cr composition and surface hardness a9ect the formation of $MoS_2$ [27]. Chromium is not only a catalyst for the reductive reaction but is also a functional additive for decreasing the thermal conductivity. Ue greater the Cr content, the lower the thermal conductivity. Uus, it is possible that the temperature at the interface is higher for the SUS430 and SUS304 substrates, where the formation of $MoS_2$ 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

Ue e9ects of the composition, hardness and roughness of the surfaces of stainless steel on the friction induced crystal growth of 2D layered $MoS_2$ were investigated. XRD measurements indicated that $MoS_2$ crystals grew on stainless steel substrates with high Cr content and low surface hardness. Uen 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 $MoS_2$ crystal, which was confirmed by XRD di9raction and Raman spectroscopy measurements. Uese results will prove useful for optimizing the friction conditions and the quality of $MoS_2$ crystals grown by the friction induced method on stainless steel surfaces.

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