Title	その場TEM観察による2硫化モリブデン膜の歪に依存した物性に関する研究
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論 文 題 目	Study of strain dependence of physical properties in MoS_2 layers by in situ transmission electron microscopy observation
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論文の内容の要旨

Owing to the ultrathin crystal structure, two-dimensional (2D) materials, such as molybdenum disulfide (MoS_2), exhibit unique mechanical and electronic properties that make them promising for the application in electronic devices. Applying strain is an effective method to modify its properties since strain can modulate the crystal structure and electronic structure. However, experimentally investigation on atomic-scale during straining has been rarely reported. Therefore, in this thesis, we developed an in situ stretching holder for the transmission electron microscopy (TEM) observation, and investigated the strain dependence of the physical properties of MoS_2 nanosheets.

We developed an in situ stretching TEM holder, which was designed for the purpose of investigating the strain dependence of 2D materials. The stretching function is performed with the piezo actuator, which generates a displacement by applying the bias voltage and drives the deformation of the titanium plate for stretching the trench in the Si chip. Our in-situ stretching TEM holder enabled us to obtain an atomic TEM image and a linear relationship between the applied bias voltage and gap distance, indicating it is stable and effective for the TEM observation. The displacement step of the holder was measured to be 0.06 nm/mV that is applicable for stretching on atomic scale.

We performed in situ stretching TEM observations of the MoS_2 nanosheet by our stretching TEM holder, for investigating the mechanical response of MoS_2 nanosheet under stretching. The fracture process of a multilayer MoS_2 nanosheet was studied, in which the crack of the sample was propagated along with the zigzag edge layer by layer. Our results suggested that the fracture of MoS_2 nanosheet was an interlayer fracture with a zigzag propagated orientation. Additionally, we observed the rippled structure in the MoS_2 nanosheet, and investigated the structural modulation during stretching. The periodically atomic-contrast change during stretching with a 0.7% tensile strain was revealed, it was attributed to the out-of-plane displacement of the sample during stretching.

We proposed a method for the quantitatively identifying ripple structure of MoS_2 nanosheets on atomic scale. The periodical ripple structure, which formed along the armchair configuration, were observed in the MoS_2 nanosheet. According on the geometry of the rippled structure and the projective feature of TEM, we investigated the relationship between the geometric structure of the ripple and corresponding apparent strain, that the rippled can be identified on atom-scaled with high-resolution TEM (HR-TEM) images. By applying the geometric phase analysis method to the HR-TEM images of ripple structures, we obtained the corresponding apparent strain distribution and proposed that the ripple structure of the MoS_2 layers could be quantitatively estimated on the sub-nanometer scale. We experimentally observed the ripple structure of the MoS_2 layers, and analyzed the corresponding apparent strain. It was found that it was an inclined sinusoidal pattern, which is inclined approximately 7.1° from the plane perpendicular to the incident electron beam, and its period and amplitude were estimated to be 5.5 and 0.3 nm, respectively. Furthermore, the bending model of MoS_2 nanosheet was suggested to be the layer model with no-in-plane distortion, due to the van der Waals interaction between layers of MoS_2 was very weak.

We experimentally investigated the mechanical response of MoS_2 nanosheets under applied strain conditions. The geometric evolution with increasing tensile strain was revealed by using our strain-based analysis on HR-TEM images. It was found that the relationship between the tensile strain and the amplitude/period was not followed the 1/4 power scale law, indicating the continuum mechanics is failed in explaining the bending of 2D materials at the atomic scale. This failure was attributed to the incapable plate model for the bending of the 2D materials. By analyzing the strain dependence of the geometric structure of the ripples, we estimated the Poisson's ratio of MoS_2 nanosheet from our experimental results during stretching, which showed that the Poisson's ratio increased to 0.57 when the longitudinally tensile strain increased to ~1.6%. We proposed an analytical model, which revealed that the nonlinear response of Poisson's ratio with increasing strain was originated from the changing of bond length was not proportional to strain.

In conclusion, the physical properties of atomic-scale MoS_2 layers have been investigated by our homemade TEM holder. Our result revealed the interlayer fracture mechanism, proposed a strain-analysis based method to estimating rippled structure at the subnanometer scale, and investigated the strain dependence of the structure and Poisson's ratio of MoS_2 layers. Our results provide an experimental method for investigating 2D materials under strain conditions, which can contribute to a better understanding of their mechanical properties at the atomic scale and the development of their future applications.

Keywords: in situ TEM, MoS_2, stretching, rippled structure, strain dependence.

論文審査の結果の要旨

2 次元材料の構造的新奇性として、本来フラットである 2 次元材料を圧縮したり引っ張ったりすることによる波状構造（リップル構造）の形成がある。このリップル構造の振幅や周期と導入した歪みの関係が調べられているが、多くの場合は、100nm から 1μm スケールという比較的大きなスケールである。一方、理論的には、原子スケールのリップル構造が示唆されているが、それを示す実験報告はない。

本研究では、代表的な 2 次元材料である MoS_2 ナノシートを架橋し、かつ、引っ張ることが可能な Si チップ、および、この Si チップを引っ張る装置を組み合わせた透過型電子顕微鏡 (TEM) ホルダーを作製し、MoS_2 ナノシートがもつ原子スケールのリップル構造の観測を目的とした。MoS_2 ナノシートは、引張りに対してエネルギーギャップが小さくなるといった電子状態の歪依存性が指摘されている。

実験では、バルク MoS_2 結晶から機械的剥離によってナノシートを得、リソグラフィーで作製した Si チップに転写した。観察は、材料表面の汚染を避けるため超高真空 TEM で行った。TEM 像は、動画で収録し、ピエゾによる引張りでナノシートの構造変化を捉えた。なお、ピエゾの印加電圧と引張り歪

の関係は、予め計測しており、ほぼ線形の関係であることを確認している。

得られた TEM 像から、リップル構造に相当すると思われる周期的な像コントラストの変調があることを見出した。そこで、幾何学的位相解析（GPA）法を用いて TEM 像を解析することにより、リップル構造の周期と振幅などを推定する手法を検討した。その結果、観測した MoS_2 ナノシートが電子線法に対し垂直から 7.1 度傾いていること、また、周期と振幅がそれぞれ 5.3 nm と 0.3 nm であることが分かった。この結果は、原子スケールの振幅をもつリップル構造の存在を示している。

さらに、同じナノシートを引っ張ることによって変化するリップル構造について、引張り歪み 0.26%, 0.51%, 0.77%, and 1.02%で得た TEM 像から GPA 法を用いて周期と振幅を推定し、歪依存性を得た。この結果、ポアッソン比は 1%の引張り歪までほぼ一定値であるが、それ以上の歪で上昇することが分かった。このようなポアッソン比の振る舞いは、MoS_2 構造の原子間結合長や結合角度の歪依存性で説明でき、その説明は機械的応答が非線形であることを示していた。

以上、本論文は、引っ張る装置を組み合わせた TEM ホルダーを作製し、MoS_2 ナノシートの原子スケールのリップル構造を明らかにし、さらに、そのリップル構造の引張り歪依存性から MoS_2 ナノシートの非線形な機械的応答を見出しており、学術的に貢献するところが大きい。よって博士（マテリアルサイエンス）の学位論文として十分価値あるものと認めた。