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論　文　題　目	水晶振動子力センサーを組み込んだ透過型電子顕微鏡法による金ナノ接点の機械特性の研究			
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論文の内容の要旨

Mechanical properties of nano-contacts (NCs) have attracted much interest, which are expected to exhibit dependence on size, shape and crystal orientation. In particular, the deformation process and Young's modulus of metal NCs would be important issues for not only science but also industry, but they have not been understood fully. Molecular dynamical calculation suggested that some specific structural transformation occurred by stretching the metal NC. Experimentally, it was observed that the shape of metal constriction depended on the stretching process and the long neck could be formed when its crystalline quality was high. Also, Young's modules of silver and zinc oxide nanomaterials have been measured to differ from their bulk values. These experimental results could be supported by the numerical calculation. On the other hand, in gold NCs, experimental results have been rarely obtained, and first-principles calculation has some difficulties due to heavy element. In order to investigate the mechanical properties of nanomaterials, it is beneficial to use an in-situ TEM method combined with a force sensor, called TEM-AFM method, because the shape and size of nanomaterials can be evaluated. In previous TEM-AFM methods, the loading force was evaluated from the bending of a Si cantilever, and the displacement of a sample was measured in the TEM observation. However, it seemed difficult to precisely estimate the displacement, because it was too small (below a few percent of sample length) to precisely be measured in the TEM image. Also, even if increasing the displacement avoid this problem, the large displacement leads to difficulty in TEM observation with atomic-resolution during measurement.

In this study, I developed a TEM holder equipped with a quartz length extension resonator (LER) as a force sensor. The LER with high effective stiffness (e.g., ~ 10^6 N/m) has an advantage in frequency modulation detection mode. It can measure the equivalent spring constant or force gradient of metal NC under strain associated with an oscillation amplitude of the order of several tens pm. Under such small oscillation amplitude, plastic deformation of gold NC or distortion of TEM image can be avoided.

I established an evaluation method of the effective spring constant of the LER. For quantitative measurement, it is critical to estimate the relationship between the LER oscillation amplitude and the electrical signal associated with the oscillation due to piezoelectric effect, called the sensitivity of LER. I found that Fourier transformation pattern of the TEM image shows modulation as if multiplied by the Bessel function corresponding to the oscillation amplitude. In this finding, the sensitivity of LER could be estimated precisely. The effective spring constant could be determined by fitting the thermal oscillation spectrum of LER with the theoretical formula, since the sensitivity has already been determined.

The equivalent spring constant and electrical conductance of the gold NC were measured simultaneously with TEM observation during the thinning process of the gold NC. The shift of the resonance frequency (Δf) could be expressed by $\Delta f = k_{\mathrm{ts}}(Q_0) \times f_0/2k$, assuming that the equivalent spring constant of gold NC ($k_{\mathrm{ts}}(Q)$) around the center of oscillation Q_0 is approximated by a linear function of the displacement, $k_s(Q) = \alpha(Q - Q_0) + k_{\mathrm{ts}}(Q_0)$, where f_0 is the resonance frequency without gold NC, and k is the effective spring constant of LER. The cross section of the gold NC, which cannot be measured directly in the TEM image, could be estimated by the electrical conductance. The experimental results suggested that gold NC (a part of narrow constriction) tends to have almost the same length and cross-sectional area by thinning, which depends on the stretching direction. Since the measured spring constant can be regarded as a series coupling of the springs of the gold NC and the bases supporting the Au NC, it is necessary to obtain the contribution of the gold NC from the measured spring constant for estimating the Young's modulus. I tried to estimate the Young's modulus of the gold NC by assuming that the thinning process of the gold NC can be described by a simple deformation model. In this estimation, the shape was evaluated by the TEM image and electrical conductance value. Young's modulus for gold NC was suggested to depend on the stretching directions. However, Young's modulus of gold NC did not seem to depend on the size of NC. The specificity of Young's modulus of gold NC may depend on the structure of the NC rather than the size.

In conclusion, I developed the newly in-situ TEM method utilizing quartz resonator force sensor which enables us to estimate mechanical properties of single-nanometer-scale materials. Using this method, I could clarify the deformation process and Young's modulus of gold NC.

Keywords: nano-contact, nano-mechanics, in-situ TEM, frequency modulation AFM, length extension resonator

論文審査の結果の要旨

金属と金属の接触によって生じるナノ接点の機械的性質は、摩擦や摩耗を理解する第一歩として重要であるが、あまり明らかになっていない。理論計算によってヤング率や降伏応力がサイズ、形状、結晶方位などに依存することが示されているが、結晶構造と機械的性質の関係を直接調べる実験手法が確立されていない点に課題がある。本研究は、長辺振動水晶振動子（LER）という高感度力センサーを備えた透過型電子顕微鏡（TEM）ホルダーを開発することで、金属ナノ接点の構造とそのばね定数を同時に計測し、金属ナノ接点のヤング率を評価することを目的とした。LER は、有効ばね定数が非常に高い（～10^6 N/m）ため、わずか数十 pm オーダーの振幅で振動させ、周波数変調検出モードで LER に接触している金属接点の等価ばね定数または力勾配を測定できるという利点を持つ。

金属接点の等価ばね定数を高い精度で計測するには、LER のばね定数を正確に評価する必要がある。この評価のため TEM 像を用いた振動測定法を確立した。振動しているサンプル

を撮像した TEM 画像のフーリエ変換パターンは、振動振幅に対応するベッセル関数を掛けたような変調を示していることを見出した。この関係から LER の振幅を評価することで、圧電効果による電気信号と変位の関係（変位検出感度）を得ることができた。さらに、変位検出感度と LER の熱振動スペクトルを理論式に当てはめることで、LER のばね定数を正確に評価した。

ヤング率測定は、金ナノ接点を対象に行った。測定から得たばね定数は、金ナノ接点とそれを担持する基板のそれぞれからの寄与がある。ナノ接点が太い場合、基板の寄与が大きく、細い場合、ナノ接点の寄与が大きい。金接点を[110]方位に引っ張ると円柱状のナノ接点が形成することから、この円柱状ナノ接点が形成する前に測定したばね定数を基板の寄与とみなし、それ以降に形成した円柱状ナノ接点のばね定数を求めた。TEM 像とコンダクタンスから対応する金ナノ接点の形状を評価することで、金[110]ナノ接点のヤング率がおよそ 80GPa であることを見出した。この値は、バルク値とほぼ同じである。また、[001]方位や[111]方位に引っ張ることにより形成した金ナノ接点のヤング率も評価した。特に、金[001]ナノ接点のヤング率はバルク値の 2 倍程であることを見出した。

以上、本論文は、金属ナノ接点の機械的性質について測定装置を開発することで形状や方位に依存したヤング率を明らかにしたものであり、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。