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Experimental Evidence for Temperature Dependence of Adsorbate-induced Scattering in Metal Nanosheets and Its Implication to Gas Sensing Applications

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Abstract

The adsorption of gas molecules to metal nanosheets induces an increase in metal resistivity. However, the desorption of adsorbates at higher temperature makes it difficult to investigate the temperature dependence of adsorbate-induced carrier scattering. In this study, by utilizing stable Au-thiol bonding, we demonstrate, for the first time, that the adsorbate-induced resistivity change ($\Delta\rho_{ad}$) in metal (Au) nanosheets increases as temperature increases from 5 to 250 K. At temperatures higher than 250 K, $\Delta\rho_{ad}$ saturates and is independent of temperature. We consider that $\Delta\rho_{ad}$ originates from limited unoccupied states of adsorbates near the Fermi level. These results will be indispensable to design and evaluate the performance of metal nanosheet gas sensors, which will be useful in the IoT era.

1. Introduction

It is widely known that adsorption of gas molecules to metal thin film increases its resistivity [1]. This property has been applied to gas sensors [2]. Regarding sensor applications, it is important to establish an analytical model which predicts molecular species and their concentration from the resistance change (ΔR). However, quantitative relationship between resistance change and surface coverage has not been adequately investigated. Furthermore, since the coverage of adsorbate is influenced by temperature, little has been reported on the temperature dependence of resistivity change by adsorbates. The temperature dependence is a key for understanding the sensing mechanisms and designing practical sensors.

In this study, to realize the stable coverage of adsorbates with respect to the temperature variation, we utilized the self-assembled monolayers (SAM) as adsorbates. The thiolate-SAM adsorbed on Au films is effective for keeping adsorption density over a long time and a wide temperature range. Thus, the temperature (T) dependence of resistivity in nanosheets with and without SAM can be evaluated from 5 K to 375 K. Hence, we discussed the additional surface scattering term due to SAM modification (**Fig. 1**).

2. Experimental Section

20-nm-thick Au nanosheets without any adhesion layer were deposited on Si/SiO_2 substrate by electron-beam evaporation after Au electrode (5 nm Cr; 60 nm Au) formation. **Fig. 2**(a) shows the schematic diagram of the device structure. The film thickness was measured by TEM (**Fig. 2**(b)), and the elements in Au layer were quantitatively analyzed by EDX, indicating little impurities in the nanosheets (**Fig. 2**(c)).

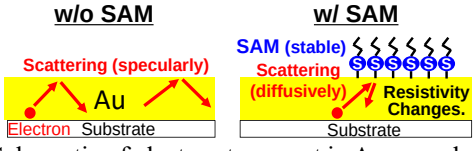

Fig. 1: Schematic of electron transport in Au nanosheets with and without SAM. (left: w/o SAM, right: w/ SAM)

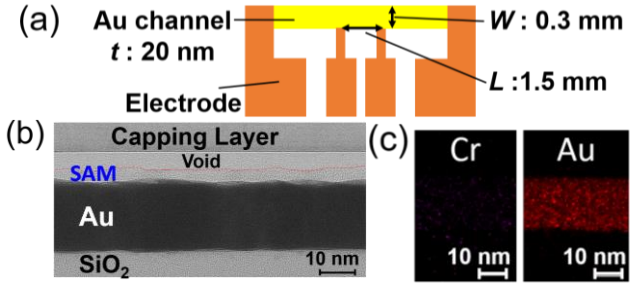

Fig. 2: (a) Four-terminal structure of the fabricated device. (b) Cross-sectional image of the nanosheet taken by TEM. The thickness of the Au layer was measured as 20 nm. (c) EDX results showing little impurities.

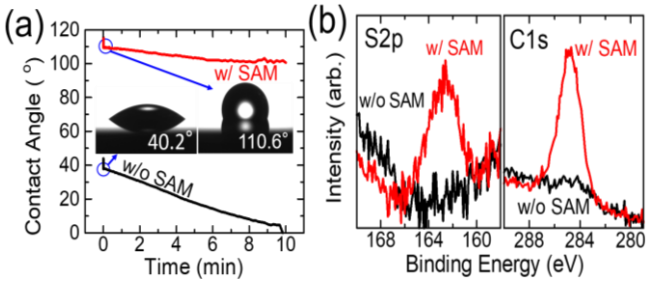

Fig. 3: (a) Time changes in contact angle before (w/o SAM) and after SAM modification (w/ SAM) on Au nanosheet. (b) XPS spectra for S2p and C1s.

The Au nanosheets were immersed at 28 ℃ into a freshly prepared solution of 1-Octadecanethiol ($CH_3(CH_2)_{17}SH$: 1-ODT) in ethanol solvent at a concentration of 1mM for 8h. The successful adsorption of SAM was confirmed using contact angle measurement and XPS. The contact angles before (w/o SAM) and after SAM modification (w/ SAM) agreed with the literature values, which suggests that SAM was chemically adsorbed on Au surface (**Fig. 3**(a)) [3,4]. The XPS analysis also indicated 1-ODT was properly adsorbed on Au surface (**Fig. 3**(b)).

The resistivity of Au nanosheets with and without SAM were measured using physical property measurement system (PPMS) in the range of temperature between 5 K and 375 K.

3. Results and Discussion

Fig. 4 shows the T dependence of resistivity in a 20-nm Au nanosheet with ($\rho_{w/\ SAM}$) and without SAM ($\rho_{w/o\ SAM}$) modification. The adsorption of SAM on the Au nanosheet results in the 2% increase in ρ. The increase of the resistivity $\Delta\rho_{ad}$ due to the adsorption of SAM is also plotted in **Fig. 4**. As

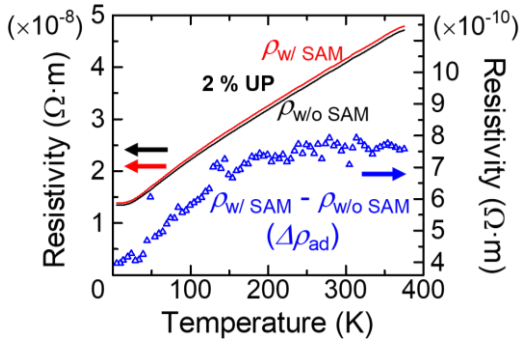

Fig. 4: Temperature dependence of resistivity of Au nanosheet with and without SAM. The resistivity increases due to SAM modification.

shown in the figure, at temperatures from 5 to 250 K $\Delta\rho_{ad}$ increases as temperature increases, and it does not depend on temperature above 250 K. This clearly demonstrates that surface scattering by SAM on Au thin films depends on temperature. We consider that the temperature-dependent scattering originates from unoccupied states of the adsorbates (sulfur) near the Fermi level of the metal (**Fig. 5**) [5]. The density of unoccupied states near the Fermi level of the metal that can be used as 'final states' increases at higher temperatures, which leads to an enhancement of the scattering rate and results in resistivity increase. We consider that the saturation of $\Delta\rho_{ad}$ is due to the absence of available unoccupied DOS of 1-ODT at temperatures higher than 250 K.

In order to confirm the validity of change in resistivity by SAM modification, we calculated the temperature dependence of resistivity of a 20-nm Au nanosheet ($\rho_{w/o\ SAM}$) based on a Bloch-Grüneisen theory and a Fuchs-Sondheimer (FS) + Mayadas-Shatzkes (MS) models [6,7]. In the FS + MS models, the effect of electron-surface scattering on the resistivity is introduced through specularity parameters "P" and "Q", associated with the upper (free surface) and the lower (metal-substrate) interfaces, respectively. **Fig. 6** shows the calculated results with P, Q, and Θ_D as fitting parameters. The results agreed well with the experimental values when we set P = 0.41, Q = 0.9, and Θ_D = 150 K.

Next, we calculated the resistivity increase by SAM modification ($\Delta\rho_{ad}$) as shown in **Fig. 7**(a). The temperature dependence of $\Delta\rho_{ad}$ is best fitted by introducing temperature dependence into specularity parameter P; this trend cannot be reproduced by temperature-independent P (The black line in **Fig. 7**(a)). The changes in P as a function of temperature are plotted in **Fig. 7**(b), showing that P is decreased in the amount of 0.036 from 5 K to 375 K. To understand quantitatively the

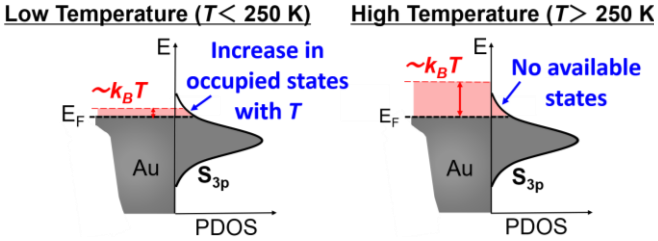

Fig. 5: Projected density of states (PDOS) induced by a S atom. Number of occupied states depend on temperature.

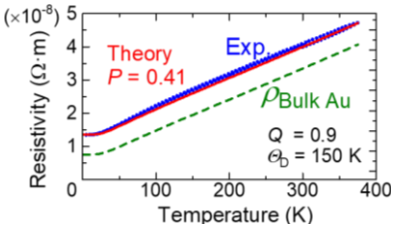

Fig. 6: Experimental and calculated resistivity of a 20-nm Au nanosheet ($\rho_{w/o\ SAM}$) as a function of temperature. The resistivity of bulk Au [6] is also shown as a reference.

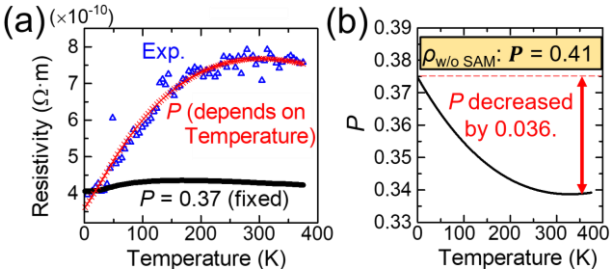

Fig. 7: (a) Fitting results of the increment of resistivity by SAM modification $\Delta\rho_{ad}$ using FS + MS model with Temperature-dependent P. Black line is the ones with fixed P (P = 0.37). (b) Temperature dependence of P showing P decreased by 0.036 in the range of temperature between 5 K and 375 K.

relationship between T-dependent change in P and the DOS of adsorbates at the Fermi level, additional work is needed.

It should be noted that, in conventional electrical gas sensors, the ratio of resistance change, $\Delta R/R$, is used as the indicator of gas concentration. However, our work suggests that ΔR can be used as a temperature-independent indicator of concentration, since ΔR is saturated at higher temperatures.

4. Conclusions

We demonstrated, for the first time, that the resistivity increase in Au nanosheets by thiol adsorption ($\Delta\rho_{ad}$) is enhanced from 5 to 250 K, and $\Delta\rho_{ad}$ is saturated above 250 K. Furthermore, the temperature dependence of $\Delta\rho_{ad}$ can be explained by introducing temperature dependence into specularity parameter P. We consider that these trends originate from the unoccupied states of adsorbates near the Fermi level. We consider that the sensor response of metal nanosheets could be predicted by calculating the PDOS of adsorbates. These results will be indispensable to design and evaluate the performance of metal nanosheet gas sensors, which will be useful in the IoT era.

Acknowledgements

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