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Spatial Variation of the Work Function in Nano-crystalline TiN Films Measured by Dual-Mode Scanning Tunneling Microscopy

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Abstract

Nano-crystalline TiN films are important electrode materials for technology of energy-efficient CMOS and fuel cells. One of the critical issue is work function (WF) variations for electrodes made of sub-30-nm TiN grains. In the paper we explored novel approach to attain a spatial resolution of ~1 nm for WF mapping by using combined measurements of tunneling current and interaction force in scanning tunneling microscopy. Three types of TiN crystal planes with different work functions were identified. Upon the film annealing at 800°C in N_2 atmosphere, the mean grain size increased from 3-5 nm to 20-30 nm. Statistical analysis showed that TiN crystal planes with a low work function covered ~56% of the surface, and were ascribed to (111) planes of cubic TiN crystal.

1. Introduction

TiN films are used as a gate electrode in modern FET devices. It was demonstrated that the threshold-voltage variability of advanced FET devices caused in part by work function variation in granular TiN gate electrodes.[1] As TiN films consist of small grains with a size of 3-20 nm and different crystal orientations,[2] random distribution of the nano-crystals causes work function (WF) variation along the film. Therefore, measurements of the WF variation for individual TiN grains with high spatial resolution are an important challenge.

In this paper we demonstrate novel approach to distinguish TiN grains with different WF by using dual-mode measurements of tunneling current and interaction force acting on the probe of a scanning tunneling microscope (STM). By monitoring the force change due to the tunneling barrier conductance, we were able to recognize TiN facets with different WF for the grains down to 3 nm in size. Statistical analysis revealed 3 types of grains with different WF values, and the large area fraction of grains with low WF for a 20-nm-thick TiN film annealed in N_2 at 800°C.

2. Results and Discussion

Dual-mode measurement method

The principle of the method is based on the relationship between tunneling current and probe-to-sample tunneling gap under a bias voltage (V_S). Assuming a rectangular potential barrier between the STM probe and the sample surface, mean tunneling current vs. the gap distance (Z) is approximated as

$$I_{tun}(Z) \propto Exp\left[-A\sqrt{\langle\Phi\rangle}\cdot Z\right] \qquad (1)$$

where A is a dimensional constant. The effective barrier height is given by

$$\langle\Phi\rangle = \frac{\varphi_{tip} + WF}{2} - \frac{qV_s}{2} - \Delta\phi_{im} \qquad (2)$$

and the image potential ($\Delta\phi_{im}$). When the work function of the STM tip (φ_{tip}) and V_s are kept constant, eq. (1) predicts steep current change with Z for larger WF. Thus, to maintain the predefined onset current (I_{set}) in the STM mode the tunneling gap is adjusted. Therefore, spatial variation of the WF is obtained by monitoring the gap distance.

In our setup, change of the gap distance causes a shift in the resonance frequency (Δf) of the vibrating STM probe attached to a quartz force sensor (qLER).[3] Thus, simultaneous measurements of the constant current STM topograph and corresponding Δf map allows us to recognize TiN planes with different WF.

Fig.1 illustrates the method where $I_{tun}(Z)$ curves were measured for two TiN grains at the same probe-sample gap in the constant force mode. The current rise is steep for grain “2”, indicating $WF(2) > WF(1)$. To maintain $I_{set} = 30\,pA$ in the STM mode, the STM probe must stay close to the sample surface by 300 pm for grain “2”, which results in stronger interaction compared to that for a grain “1”. For $V_s = 0.9\,V$, we obtained $\Delta f = +7\,Hz$ for grain “2”, and $\Delta f = -4\,Hz$ for grain “1”.

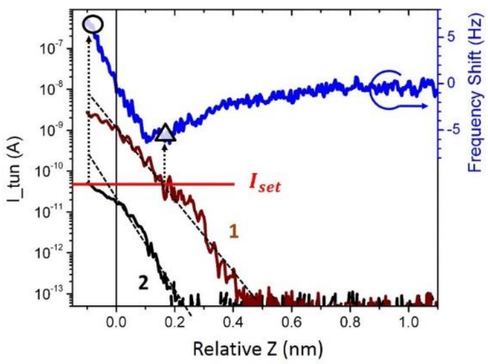

Fig. 1 Log tunneling current and frequency shift vs. gap distance for 2 grains obtained with Vs=0.9V, $\Delta f = 1Hz$, and an oscillation amplitude of 150 pm. Symbols indicate Δf values when I_{set} maintained constant.

Surface morphology

Fig.2(a) shows the STM topograph of nanocrystalline TiN film with a nominal thickness of 20 nm which was processed at 800^{o}C in N_2 gas for 2h. The STM measurements were done after surface cleaning by annealing at 300^{o}C in UHV conditions. Dozens of small grains of 20-30 nm in size and ~3 nm in height are randomly oriented in agreement with TEM data (not shown). In comparison, the mean gain size was 3-5 nm for unprocessed films.

TiN work function maps

TiN grains with different WF appeared as areas of blue, green and red color in the corresponding Δf map in Fig. 2(b). Two TiN planes of a grain in bottom-right corner indicated in Fig.2(a,b) by triangular shapes had similar WF, but a grain in center-left side in the images had low WF.

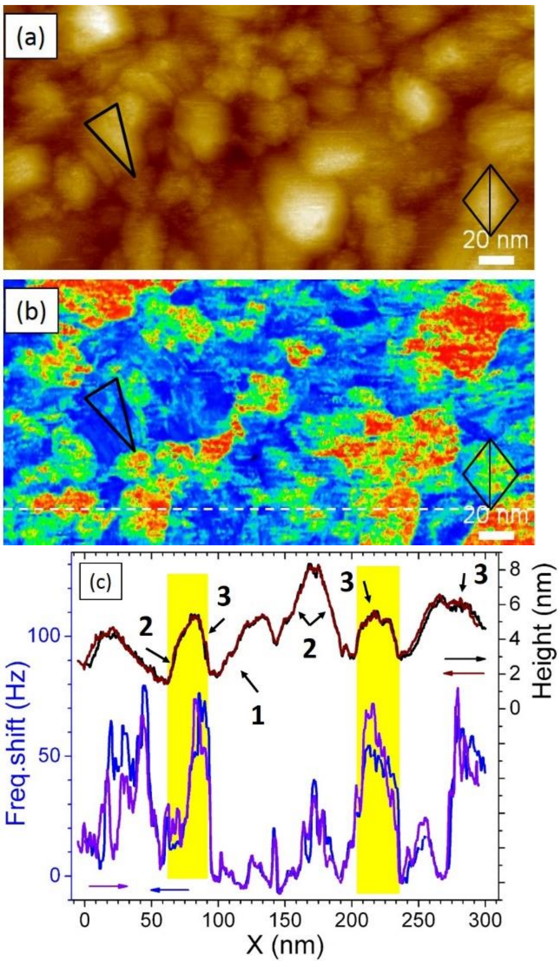

Fig. 2 (a) STM topograph and (b) corresponding Δf map of TiN nanocrystals measured with $I_{set} = 5\,pA, V_s = 0.9V$. The color scale is 5 nm in (a) and 0(blue) – 50(red) Hz in (b). Triangular shapes mark different crystal facets. (c) Line profiles from (a) and (b) for left-to-right and right-to-left scan directions at a position marked by broken lines in (b). Numbers indicate different WF type.

Line profiles in Fig.2 showed (i) the reproducibility of the Δf variation, and (ii) abrupt change of Δf within 1 nm across boundaries between grains seen at positions of X=95, 230 and 280 nm. We see that 2 grains indicated by yellow bars had similar Δf for different crystal plane slopes. Also, a grain at a position of 60-95 nm showed three facets with two Δf values. As seen at X= 20-50 nm in Fig.2(c), small surface steps in the height profiles coincided with spikes in the Δf value, which suggest the influence of the surface step dipole on the measured WF as reported previously for different metal surfaces.[4] Our observations indicate that the Δf change was caused primarily by the WF of TiN crystal planes rather than the grain shape.

Area fraction of TiN work function

To evaluate the area fraction of TiN facets with different WF, we analyzed histograms obtained from Δf maps. Fig.3 shows an example of the data for Fig.2(b), where a narrow peak near $\Delta f = 0\,Hz$ represented a fraction of low-WF facets, and a broad distribution below 80 Hz was a fraction of high-WF facets. The best fit of the distribution was obtained assuming three WF values where the area fraction was about 28% for type 1 ($\Delta f = 0\,Hz$), ~28% for type 2, and ~44% for type 3. Similar values we obtained in 2 other regions. Growth of TiN crystals at 800^{o}C in N_2 gas is expected to produce polar (111)-N planes with a low WF (type 1) and a pyramidal shape as seen in Fig.2(a). Other TiN planes were attributed to (111)-Ti planes (type2) and to non-polar (200) crystal plains with a high-WF (type 3).

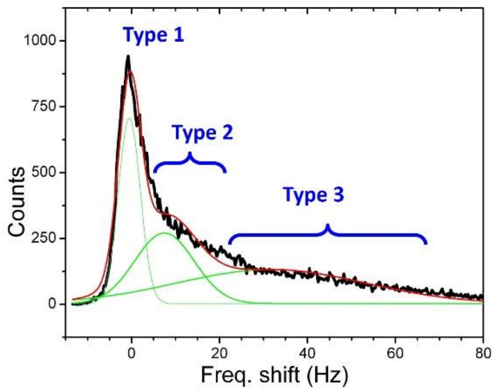

Fig. 3 A histogram of Δf occurrence for Fig.2(b). Green lines are the best fit with 3 Lorentz curves.

3. Conclusions

By employing the dual-mode STM measurements, we are able to obtain spatial distributions of the WF in nanocrystalline TiN films with an effective spatial resolution of ~1 nm, and the enhanced sensitivity to WF variations. Crystal planes with low WF values covered ~56% of TiN film processed at 800^{o}C in N_2.

References

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