Quantum interference depression in thin metal films with nanostructured surfaces

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1. Introduction

Thanks to recent developments in nanoelectronics, devices such as superlattices, quantum wells, and others, based on the wave properties of electrons are being fabricated.[1] Under certain conditions an electron in a solid can be regarded as a plane wave. The main requirement is that at least one dimension of the solid should be less than the mean free path of the electron. In this case, the electron can move without scattering and could be regarded as de Broglie wave. Transport properties of solids such as current and heat transport are defined by electrons having energies close to the Fermi level, and the mean free path is given for those electrons. Other free electrons inside solids, for example ones having energies below the Fermi level, do not participate in current and heat transport, they are quantum mechanically forbidden to exchange energy with the environment, and hence the mean free path of such electrons is effectively infinite. Such electrons will remain ballistic inside relatively large structures.

In this work we use the wave properties of such electrons to understand the electronic structure of a solid. We analyse what happens when regular indentations, which cause interference of the de Broglie waves, are fabricated on the surface of a thin metal film. We have shown that modifying the wall of a rectangular potential energy box leads to a quantum interference depression (QID), in other words reduction of the density of quantum states for the electron.[2] The Fermi vector and Fermi energy of the thin metal increase, and consequently its work function (the difference between the vacuum and Fermi energy levels) decreases. The influence of irregularities of the thin metal films, such as grains inside the film and the surface roughness of the film, were studied in this work.

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[1] M.H. Upton et al., *Phys. Rev. Lett.* 93, 026802 (2004).

[2] A. Tavkhelidze et al., *J. Vac. Sci. Technol.* B 25 (2007) 1270.

Nanotechnology Perceptions **4** (2008) 25–28
Received 23 October 2007

Thin metal films of Au and Cr were grown using exploding wire evaporation and quench condensation both on cooled and room temperature substrates. The electron beam evaporation method was used for Nb and Au films. Work function reduction was measured in Au, Nb, Cr and SiO_2 thin films. Experimental results were interpreted as a limitation of the QID effect by film irregularities.

In this work we used the wave properties of ballistic electrons to understand the electronic structure of a solid in a way that the work function of the solid may be reduced and regulated by altering the structure. Such materials should find many applications in devices based on electron emission and electron tunnelling, and in the semiconductor industry.

2. Sample preparation

Substrates were prepared at NIL Technology (NILT) by growing a 50 nm thick thermal oxide on standard four inch silicon wafers.[3] The oxide was grown by a dry process at 1000 °C. The surface roughness R_a of the oxide surface was measured to be 0.2 nm, comparable to the measured roughness of a blank silicon wafer. In order to align the metal pads to the nano-indented areas, alignment marks were defined in the oxide film by standard u.v. lithography and 12.5% BHF (buffered hydrofluoric acid) etching. The nano-indented areas were defined by 100 kV electron beam lithography (Jeol JBX9300FS) in a 55 nm thick spin-coated ZEP520A film developed in ZEP-N50 developer. After development of the ZEP520A, any residual resist at the bottoms of the nano-indented areas was removed by a low power oxygen plasma with a resist etch rate of 10 nm/min in a resist barrel asher, in order to ensure that the thermal oxide was equally exposed to the BHF in the subsequent transfer of the nano-indented pattern the thermal oxide. The nano-indentations were transferred into the thermal oxide by a 15 s dip in 4.2% BHF solution using the ZEP520A as the masking material. A 15 s dip corresponds to a measured etch depth of approximately 8 nm (measured by a Veeco Dimension 3100 atomic force microscope). After transferring the nano-indented areas into the thermal oxide any remaining ZEP520A was removed with the oxygen plasma and the substrates were cleaned according to a Radio Corporation of America (RCA) procedure: $NH_4OH:H_2O_2:H_2O$ at 80 °C and $HCl:H_2O_2:H_2O$ at 80 °C. Finally the metal pads were defined by standard u.v. lithography, electron beam metal evaporation and lift-off. 30 Å of Ti was deposited as an adhesion layer for 600 Å Au: the last step was the gold film deposition on the substrate at room temperature (Fig. 1).[4]

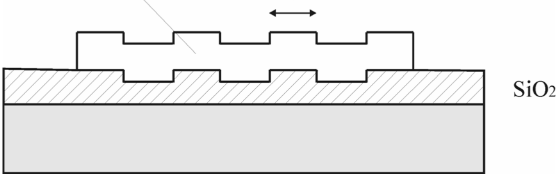

Figure 1. Schematic cross sections of the test samples.

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[3] www.nilt.com

[4] For a general introduction to these processes, see A.G. Mamalis et al., Micro and nanoprocessing techniques and applications *Nanotechnology Perceptions* 1 (2005) 31–52.

At Tbilisi State University (TSU), standard 2 inch Si wafers with thermally grown 50 nm dry oxide were used as substrata. After a conventional cleaning procedure, a layer of S1813 photoresist of thickness 0.6 μm was spun on at 4000 r.p.m. An MII-4 interference microscope was used for thickness control. Periodic lines 0.8 μm wide were created in the photoresist using u.v. photolithography, and the SiO_2 was etched using $NH_4F:HF:H_2O$, at a rate of 1 nm/s to a depth of 5–10 nm. The photoresist was then removed using acetone followed by a conventional cleaning procedure. A further layer of photoresist was attached, and another photolithographic step was used to form large structures using a lift-off process. Metal films of Au, Cr, and Nb were deposited on the substrata in a vacuum of $2–5\ 10^{-6}$ Torr (Fig. 1). Au and Cr were evaporated using rapid vacuum evaporation and quench condensing. Nb was deposited using e-beam evaporation. The thickness of the films was 20–100 nm. Substratum temperatures were 245–250 K for Au, 90–140 K for Cr, and 90–170 K for Nb. Film growth rates were 20 nm/s for Au, 1.5 nm/s for Cr, and 0.3 nm/sec for Nb.

3. Measurement results and discussion

Measurements of the work function were made using the Kelvin probe (KP) method. The method is based on measurement of the internal contact potential difference by capacitance (probe-sample capacitance) modulation. The charge reading is used to determine the contact potential difference. All measurements were comparative in order to obviate absolute inaccuracies: the difference between KP readings on a plain region of the film was compared with the reading from the ridged region of the film.

For all samples measured, the ridged regions showed a reduced work function (WF) compared with the plain regions. The magnitude of this reduction of the WF, $\Delta\phi$, depended on the structure of the film and the width of the indentations (at fixed indent depth). $\Delta\phi$ was in the range of 0.15–0.33 eV for Au, 0.3–0.42 eV for Cr and 0.15–0.32 eV for Nb. Metal films (Au, Cr, and Nb) deposited at low temperature on the substratum always showed higher $\Delta\phi$ than the same films deposited at room temperature. A low temperature reduced the mobility of the metal atoms on the substratum during deposition and resulted in a smaller grain size and a more amorphous structure of the film.[5] Grain size limits the waveband of QID. Electrons may be regarded as localized inside the grains, if their de Broglie wavelength λ is less than the grain diameter d. In the case $\lambda > d$, free electrons belong to all grains simultaneously, and boundary conditions are defined by the indented geometry of the film, while for electrons with $\lambda < d$ boundary conditions are defined by the particular grain. Therefore, grain size defines the critical de Broglie wavelength $\lambda_c = d$, below which QID is suppressed. Consequently, the QID waveband depends on grain size, which itself depends on the temperature of the substratum during deposition and film growth rate. Experiments showed higher values of QID for films with smaller grain size (lower substratum temperature).

In order to measure the dependence of $\Delta\phi$ on indentation width w, samples containing areas with different w were prepared on the same substratum. Wafers with a ridged SiO_2 layer having an indentation depth of $a = 8$ nm were prepared at NILT. Indentation width was in the range $w = 0.2–3$ μm. Au film was e-beam deposited at room temperature at NILT. Another Au film was

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[5] N.G. Semaltianos and E.G. Wilson, *Thin Solid Films* 366 (2000) 111.

deposited on the same substratum at TSU using rapid thermal evaporation and quench condensation at $T = 245$ K. The TSU films grown on a cold substratum show a greater reduction in WF. No peak was observed in $\Delta\phi(w)$ for Cr films deposited on the same substratum. The increase of $\Delta\phi(w)$ was observed in Cr films below 0.4 μm.

Our explanation of the peak in the Au films is that the electron energy distribution in granular films strongly deviates from the Fermi function. Particularly, there is a large peak at energies 5–6 eV below the Fermi level in the electron energy distribution of Au films.[6] When indentation width w matches the de Broglie wavelength of those electrons forming the peak in the energy distribution, the QID effect influences the peak region and causes most of the reduction in the WF. In another words, quantum states become forbidden in the energy region where large numbers of electrons are concentrated, resulting in an increase in the Fermi level and a corresponding reduction in the WF.

The dependence of the WF reduction on indentation depth $\Delta\phi(a)$ was studied in our previous experiments,[7] and also shows qualitative agreement with the theory.

At Portland State University (PSU), images were collected using a high resolution photoelectron microscope. Figure 2 shows the photoelectron emission microscopy (PEEM) image of 16 squares of dimensions 20 × 20 μm. Some squares have indented surfaces and others have plain surfaces. Indented and plain areas are placed in a chessboard pattern. The intensity of the image is proportional to the electron emission. Indented areas appear brighter, corresponding to more electron emission, implying a lower WF.

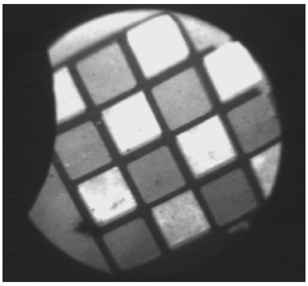

Figure 2. PEEM image of sample. Rectangular areas are arranged like a chess board. Bright squares correspond to indented areas and darker squares correspond to flat gold film.

4. Conclusions

Quantum interference depression in thin metal films depends on the film internal structure and the width of the ridges. Grain size and the de Broglie wavelength distribution of the electrons determine the optimum ridge width to set the Fermi level. The Fermi energy increase due to QID can be used in devices using internal contact potential difference, such as Schottky diodes, and in metal/semiconductor ohmic contacts for power electronics.

Acknowledgment

The work was financed and supported by Borealis Technical Ltd, assignee of certain corresponding U.S. patents (7,166,786; 7,074,498; 6,281,514; 6,495,843; 6,680,214; 6,531,703; and 6,117,344).

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[6] T.K. Sham, P.-S.G. Kim and P. Zhang, *Solid State Communications* 138 (2006) 553.

[7] A. Tavkhelidze et al., *J. Vac. Sci. Technol.* B 24 (2006) 1413.