Resistivity of thin Cu films coated with Ta, Ti, Ru, Al, and Pd barrier layers from first principles

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We present an atomistic first-principles calculation for the resistivity of rough Cu thin films coated with barrier layers of Ta, Ti, Ru, Al, and Pd. A significant difference in resistivity due to different barrier metals is found. Ti, Ta, and Ru barriers increase the resistivity whereas Al and Pd lower the resistivity, in comparison with that of bare Cu films having the same degree of roughness disorder. It is found that Al/Pd barrier atoms produce density of states (DOS) that match rather well with the DOS of Cu atoms on a Cu film with a perfectly flat surface while the DOS of Ti, Ta, and Ru do not match. Our results suggest that the geometrical roughness on the Cu film that causes diffuse scattering, can be "smoothed" out electronically by certain barriers such that the surface scattering becomes more specular.

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I. INTRODUCTION

The resistivity of Cu interconnects increases with decreasing cross section of the interconnect wire,[1] and its value more than doubles that of the bulk resistivity when the wire width is below 50 nm.[2–4] This size effect represents a great challenge for the continued down scaling of electronic devices because increased resistivity dramatically enhances heat dissipation and interconnect delay in the integrated circuits. Experimentally, among the several electron-scattering mechanisms that contribute to resistivity of Cu interconnects,[1–3,5–7] surface roughness scattering has been identified as a major source to the size effect. A 50% increase in Cu resistivity due to surface roughness scattering has been reported in a recent experimental study.[3] Since Cu wires will continue to dominate the interconnect technology in any foreseeable future, it is of critical importance to find ways to minimize roughness scattering. Experimental growth of Cu films having a perfectly flat surface has not been possible so far, as even annealed single-crystal Cu(001) layers still show a peak-to-valley roughness of more than 1 nm.[8] This geometrical disorder gives rise to a certain degree of diffuse scattering to electrons so that the resistivity is increased. By coating barrier atoms on the Cu film, the geometrical roughness may be filled by barrier atoms resulting in a smoother *geometry* thus possibly less diffuse scattering.[1] Barrier metals being examined experimentally include Ti, Ta, Ru, Al, and Pd (Refs. 1 and 9–12); results indicate that some barrier metals actually increase resistivity compared with bare Cu films while others do reduce it, and there has been little theoretical understanding of the trends.

Theoretical investigation of bulk film resistivity (as opposed to two-probe film) has a very long history starting with the well-known semiclassical model of surface roughness scattering by Fuchs[13] in 1930s and by Sondheimer[14] in 1950s. The Fuchs-Sondheimer model is still widely used by circuit engineers today. Different scattering mechanisms in metal films have also been described by empirical models[15–18] and by advanced analytic models that take into account quantum effects prevalent in very thin films.[19–21] More recently, density-functional theory (DFT) based atomic models[22,23] have been applied within the supercell approach to periodic atomic structures of Cu films. The long history and extensive investigation have provided our current understanding of thin-film resistivity. To investigate effects of barrier layers to Cu film resistivity from atomic first principles and, indeed, to investigate the disorder issues, we have recently developed a theoretical and computational formalism of nonequilibrium vertex correction (NVC),[25] and incorporated NVC into a quantum transport model based on the Keldysh nonequilibrium Green's function (NEGF) combined with DFT. The importance and the relevance of vertex corrections for transport in disordered multlayered systems have been discussed in recent works.[24,25]

In this paper, we pursue a theoretical idea that may ultimately guide the selection of barrier materials. Namely, since resistivity is a transport property which is microscopically related to the electronic structure of the material, it should be possible to "smooth" out the effects of geometrical disorder by electronic means so as to reduce the surface scattering. In other words, even though barrier atoms can fill the holes on a rough surface to make it geometrically smoother, they may not actually produce a smooth surface electronic potential to reduce scattering. Using a first-principles theoretical formalism, we have calculated resistivity of Cu thin films coated with barrier metals Ti, Ta, Ru, Al, and Pd at various coating concentrations and film thicknesses. We indeed found that Al/Pd barrier atoms produce density of states (DOS) that match very well with that of Cu atoms on a perfect Cu film, and these barriers reduce resistivity in comparison to that of bare rough Cu films. On the other hand, Ti, Ta, and Ru barrier atoms give very different DOS compared with Cu and these barriers increase resistivity. This trend is consistent with experimental observations.[1,9]

The rest of the paper is organized as follows. In the next section, we present the theoretical method used in our calculations. Section III presents the results and we conclude with a summary in Sec. IV.

II. THEORETICAL METHOD

The main advantages of the NEGF-DFT-NVC method are: (i) it is based on parameter-free atomistic first principles;

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(ii) it allows direct calculation of resistivity for two-probe structures; (iii) it provides perhaps the most efficient approach for configurational averaging of random disorder ensembles; and (iv) it allows calculations of large systems involving around several thousands of atoms for the purpose of Cu interconnect research.[26] Very briefly, in the NEGF-DFT-NVC formalism,[26] the electronic structure is determined by DFT within the tight-binding linear muffin-tin orbital (LMTO) implementation,[27] where the nonequilibrium density matrix and the transport boundary conditions of the scattering region are determined by NEGF.[28,29] The disorder configurational average of the Hamiltonian and the single-particle Green's function is carried out by the coherent-potential approximation;[30] the disorder average of the nonequilibrium density matrix is obtained using NVC.[25] For technical details of the NEGF-DFT-NVC method we refer interested readers to Ref. 25 and its associated online supplementary material.[31] After the self-consistent iteration of the NEGF-DFT-NVC calculation is converged, the disorder averaged conductance is obtained from the following expression:[25]

$$\bar{G} = \frac{e^2}{h}(\mathrm{Tr}[\Gamma_L \bar{g}^R \Gamma_R \bar{g}^A] + \mathrm{Tr}[\Gamma_L \bar{g}^R \Gamma_{\mathrm{VC}} \bar{g}^A]), \quad (1)$$

where $\bar{g}^{R,A}$ are the retarded and advanced Green's functions that have been averaged over the impurity configurations; $\Gamma_{L,R}$ are the self-energies of the left and right leads which describe interactions between the leads and the scattering region; and Γ_{VC} is the vertex correction self-energy which arises due to multiple impurity scattering of the electrons.[25,30] The trace is the summation of all the diagonal elements in the orbital space over the two-dimensional Brillouin zone sampled by $(k_x,k_y)=(60,1)$ k mesh for each energy point. All the self-consistent NEGF-DFT-NVC calculations are performed at zero temperature. For the Cu films in this work, resistances are calculated at equilibrium for different lengths (in the range from 2.55 to 8.68 nm) at a particular thickness using the Eq. (1). For all the cases, the resistance is a linear function of length l showing an Ohmic behavior,[26] and the resistivity (ρ) is therefore obtained from the slope of the linear curve. Note that we applied the equilibrium version of the NEGF-DFT-NVC theory for this particular problem where we are interested in the conductance of Cu films only at equilibrium. In this situation, NEGF $G^<$ is reduced to the retarded Green's function G^R, and the only vertex correction necessary is for the calculation of the quantity Γ_{VC} in Eq. (1).

In our calculations, the Cu film is treated as a two-probe device structure having specific thickness d and length l, as shown in Fig. 1. The two-probe structure consists of perfect left and right Cu leads plus a scattering region containing the rough Cu film. The experimental value of 3.61 Å is used for the Cu lattice constant. In our atomic model, a disordered rough surface layer of Cu means there is only x% of Cu atoms in that layer and the other $(1-x)$% of Cu atoms are missing and replaced by vacuum. The randomly missing Cu atoms provide disorder scattering to charge flow in the Cu interconnect. For barrier coated Cu films, the $(1-x)$% missing Cu atoms are replaced by the barrier metal atoms and they can be viewed as random impurities. We adopted two coating models: an one-layer model where barrier atoms are introduced only at the top layer of the Cu film; and a four-layer model where three additional pure barrier layers are deposited on top of one-layer model. To save the prohibitively large computation of relaxing atomic structures for all the possible disordered surfaces, we assume that the barrier atoms sit randomly on Cu lattice sites without structure relaxation. Namely, in the surface layer of a Cu film, a site is randomly occupied by x% probability of Cu and $(1-x)$% probability of barrier atom. This approximation is adequate for the purpose of obtaining a first qualitative trend to the barrier coating effects.

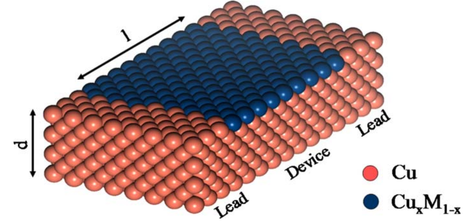

FIG. 1. (Color online) (a) Atomic structure of the Cu thin film treated as a two-probe device of length l and thickness d. It is periodic in the width direction. The leads are perfect Cu films without disorder. The crystal directions are [010] and [101] along the thickness and the length of the Cu film, respectively. The barrier metal coating is shown for the one-layer coating model. For the four-layer coating model, three additional pure metal layers are added on top of the one-layer model. The Cu-barrier interface layer is modeled by randomly replacing Cu atoms with barrier atoms of concentration $(1-x)$.

III. RESULTS AND DISCUSSION

Figure 2 plots the calculated Cu resistivity ρ as a function of film thickness d for four different barrier metals Ta, Ru, Pd, and Al, as well as rough Cu films without a barrier coating denoted by "Va." The results for Ti coating are not presented to make the plot less crowded since they are very similar to that of Ta with little difference in the resistivity values. It is clear that barrier metals make a significant difference in the resistivity. For Ta and Ru coatings, the size effect is very pronounced and the resistivity is higher than bare Cu films. On the other hand, the resistivity with Al and Pd barriers are lower than the bare Cu films (see Fig. 2). These results qualitatively agree with experimental observations where the Cu sheet resistance was reported to increase by up to 15% using Ta barrier coating;[9] and was always reduced with Al barrier coating.[1] A comparison between the two coating models (one-layer or four-layer barrier) does not show a significant qualitative difference, suggesting that the most important contribution to resistivity comes from the Cu-barrier metal interface. For all four barrier metals, the four-layer coating model has higher resistivity which can be attributed to the increased mismatch of the pure Cu leads with the thicker barrier layers in the scattering region, causing electron scattering into the barrier layer. Since there is no qualitative difference, in the following we will focus on the one-layer coating model.

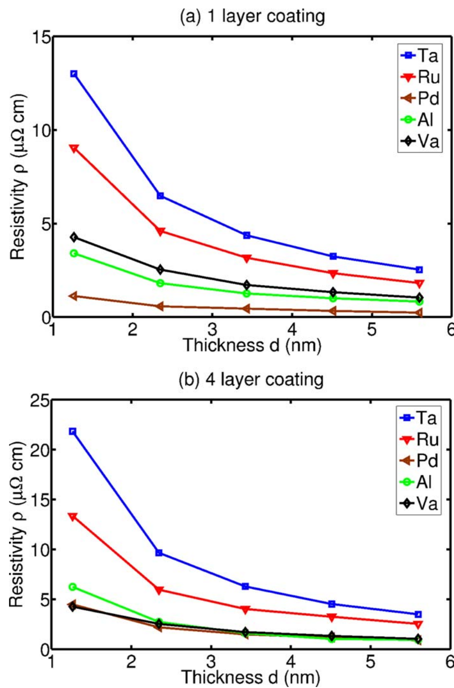

FIG. 2. (Color online) Cu thin-film resistivity ρ as a function of film thickness d for different metal barriers with concentration $x=0.9$ for the (a) one-layer and (b) the four-layer coating models. The resistivity for bare rough Cu films is denoted as Va. The maximum thickness value of $d=5.59$ nm corresponds to 31 monolayers of Cu film.

Figure 3 is a plot of the resistivity versus the disorder concentration parameter $(1-x)$ for a film of thickness $d=3.43$ nm. The resistivity is not completely symmetric around $x=0.5$ which is expected because the atomic potential of the Cu atom and the barrier atom are not the same. The maximum resistivity value is observed in the range between $x=0.5$ and 0.7 for all barriers. The resistivity is zero at both limits $x=0$ and $x=1$, where the Cu surface is perfect such that scattering is completely specular. Very importantly, for any x value the resistivity with Al and Pd barrier coating is always lower than the bare Cu film but it becomes higher with Ta and Ru barriers. These results suggest that Al and Pd barrier layers should be effective in suppressing the size effect in Cu films.

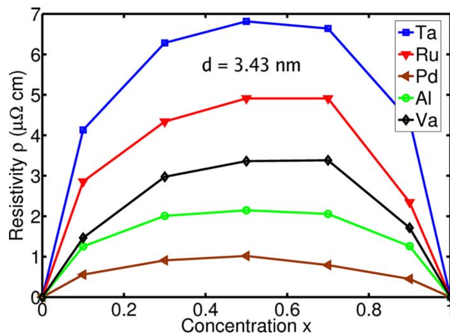

FIG. 3. (Color online) Resistivity (ρ) of Cu thin film at thickness $d=3.43$ nm and one-layer coating model versus disorder parameter x.

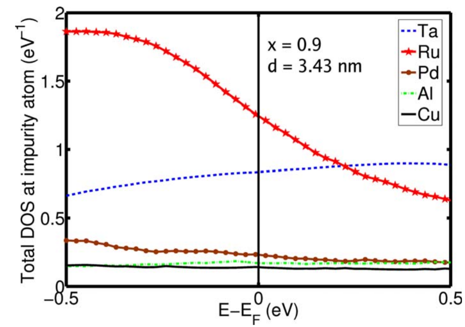

FIG. 4. (Color online) DOS as a function of energy E at the metal impurity atoms on the Cu surface. The solid line denoted by "Cu" represents the DOS for Cu atom on a perfect Cu surface without any impurity.

The effect of the barrier coating can be due to several factors including localized d states, a change in the Fermi surface and/or a difference in the lattice structure and crystal potentials. To better understand this effect, we calculated the DOS at the barrier metal atoms on the Cu-barrier interface layer. The results are presented in Fig. 4. We found that the DOS for Al/Pd match very well with that for Cu atoms on a perfect Cu surface while the DOS for Ta/Ru does not match. Therefore, the effect of Al/Pd barriers is to effectively smooth out the electronic structure of a rough Cu film toward that of a perfect film, thereby reducing the overall resistivity. For Ta/Ru barriers, even though the DOS around E_F is much higher than that for Cu, it is mostly composed of the rather localized d orbital. We may thus argue that the d states of the Ta/Ru atoms do not contribute as well to the overall conductance, and the mismatch of the DOS with that of Cu does not smooth out the electronic structure of the rough Cu film. To further confirm the behavior of DOS of Fig. 4, we have carried out additional calculations[32] using a projector-augmented wave DFT method as implemented in the electronic package VASP (Ref. 33) on *periodic* structures of the barrier coated films, and the results (not presented) show very good qualitative agreement with our two-probe results in Fig. 4.

IV. SUMMARY

In summary, we have calculated the resistivity of thin Cu films coated with several barrier metals using a self-consistent *ab initio* formalism. There is a substantial difference in resistivity for the different barriers. We found that the size effect is much more pronounced and resistivity values are higher for Ti, Ta, and Ru barriers whereas for Al and Pd the resistivity is lower than for bare Cu films. The DOS of the Al/Pd barrier atoms match very well with that of perfect Cu surface atoms while for other barrier atoms there is no match. In particular, Ta, Ti, and Ru barrier metal atoms present a localized d character around the Fermi energy which is very different from that of Cu atoms. Our results strongly suggest that it is possible to electronically smooth out the effects of roughness of thin Cu films such that the resulting Cu-barrier metal interface becomes more specular to electron scattering.

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[31] See supplementary material at http://link.aps.org/supplemental/10.1103/PhysRevLett.100.166805 for further information on the theoretical method employed in this study.
[32] For the DOS calculations with VASP, we used a supercell consists of a seven-layer (4×4)Cu(110) periodic atomic structure with one impurity metal atom replacing a Cu atom at the surface layer. The vacuum region in the z direction of the supercell is set to be around 15 Å. The four top layers are allowed to relax while the three bottom layers are fixed at the bulk position with a bulk Cu lattice constant 3.61 Å, consistent with our LMTO calculations. An energy cutoff of 275 eV is used in the plane-wave basis. The Monkhorst-Pack scheme is adopted for integration of Brillouin zone with a k mesh of $8\times8\times1$. Note that, the VASP calculations are only possible for periodic structures whereas our LMTO calculations are performed treating the Cu film as a two-probe device of specific length.
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