Determination of the Surface Conductivity of Ultrathin Metallic Films on Si(111) by High-Resolution Electron-Energy-Loss Spectroscopy

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Temperature-dependent (20–300 K) electron-energy-loss measurements of the quasielastic peak for ~2.5–10 Å of evaporated Au and Pd on Si(111) are presented, which, together with a theory of the electron scattering from metallic layers, permit the determination of dc conductivities. Metallic films, ~10 Å thick, are found to have large temperature-independent resistivities dominated by surface scattering and imperfections. An unusual temperature-dependent resistivity is found for Pd on Si which is suggested to arise from a phase transition near the interface.

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Considerable interest exists in the measurement and understanding of electrical transport phenomena in two-dimensional conducting systems.[1-4] In many circumstances studies of extremely thin metal films (<25 Å)—a regime rich in possible physical phenomena—are not easily accessible with conventional measurement methods which generally require fault-free continuous films and numerous physical contacts to the film. Such problems, for example, have limited transport studies of as-grown silicide films to thicknesses $\gtrsim 200$ Å,[5,6] and may make studies of thin metal films $\lesssim 25$ Å on even "ideal" substrates problematical.[1,2]

Here we demonstrate, for the first time, that high-resolution electron-energy-loss spectroscopy (EELS) can be used *quantitatively* to study the dc electrical conductivity of "ultrathin" (2.5–10 Å thick), high-resistivity metallic films on semiconductor or insulating surfaces. Previous EELS studies of thin metal layers on semiconductor surfaces have revealed quasielastic beam broadening and increased background scattering associated with the metallic response of the conduction electrons to the long-range Coulomb fields of the incident electron.[7,8] To obtain quantitative conductivity information we have developed a temperature-dependent multiple-excitation theory of this quasielastic beam broadening and apply it here to analyze the first temperature-dependent EELS measurements of any metallic film, i.e., Pd and Au on Si(111). We find temperature-independent surface resistivities of ~600 $\mu\Omega$ cm for 14- and 8.5-Å-thick, continuous films of Pd_2Si and Au, respectively, which indicate transport dominated by imperfections and surface scattering. However, for the Pd on Si system, an "anomalous" temperature-dependent component of the resistivity is found which strongly reduces the resistivity to ~250 $\mu\Omega$ cm below ~100 K. This enhanced conductivity appears to be associated with the metal-semiconductor interface, and we tentatively attribute it to an interface-stress-induced phase transition.

Our electron scattering studies rely on a quantitative interpretation of the width of the quasielastic peak for electrons scattered from thin metallic films on top of a low-conductivity or an insulating substrate. The electrons which contribute to the broadening of the quasielastic peak have lost or absorbed a small energy $\hbar\omega$, typically a few millielectronvolts. Thus according to dipole scattering theory[9] the momentum transfer (parallel to the surface) is very small, $q_\parallel \sim (\hbar\omega/2E_0)k \sim 10^{-4}$ Å^{-1}, and the inelastically scattered electrons form an extremely narrow lobe of width $\Delta\theta \sim \hbar\omega/2E_0 \sim 10^{-2}$ deg, centered almost in the specular direction. This small momentum transfer not only requires that multiple excitations be accounted for in any analysis but results in an averaged or "homogeneous" response of the system on a scale ~10^4 Å.

As described elsewhere[10] we have derived the equations to treat accurately the temperature-dependent quasielastic scattering from a metallic layer on a semiconductor or insulating substrate characterized by a local scalar dielectric constant, ϵ_b. From this analysis we find that the profile of the quasielastic peak, $P(\omega)$, is well approximated under our experimental conditions by

$$P(\omega)=\frac{1}{\pi}\left[\frac{\Gamma/2}{\omega^2+(\Gamma/2)^2}\right], \qquad (1)$$

where $\Gamma = 2Chk_BT$. Here

$$C=\frac{4}{\pi}\frac{1}{\cos^2\alpha}\frac{1}{ka_0}\frac{1}{\epsilon_0+1},$$

and h is a function of the angle of incidence α and of the product $\beta\tau$, with τ the Drude relaxation time for the conduction electrons in the film and $\beta = 4\pi ne^2/m^*(\epsilon_b+1)v$. Here n is the number of conduction electrons per unit film *area*, m^* their effective mass, and v the velocity of the incident electrons. The product $\beta\tau$ is thus proportional to the areal density of electrons times their mobility and thus directly related through h to the resistivity. The function h is tabulated in Ref. 10.

The detected quasielastic peak $\bar{P}(\omega)$ is obtained by convolution of (1) with the instrumental "resolution function" which is found to be a Gaussian with a full width at half maximum (FWHM) of Γ_0. From an evaluation of $\bar{P}(\omega)$ for *different temperatures* we determin the full width at half maximum which we then compare to experiment to determine the values of $\beta\tau$ at each temperature. (In principle both β and τ can be temperature dependent.)

Experimental measurements of the quasielastic peak were performed on Au and Pd films evaporated *in situ* at room temperature on Pd-impurity stabilized 1×1 Si(111) surfaces. The electron scattering conditions had $\alpha = 45°$, an incident electron energy $E_0 = 12$ eV, an analyzer acceptance angle of 2°, and a resolution (Γ_0) of 6–9 meV. The starting sample had a bulk resistivity of 15 Ω cm, with these 1×1 surfaces exhibiting negligible elastic beam broadening. All surfaces were also characterized *in situ* with LEED and uv photoemission spectroscopy (UPS). Coverage calibrations were obtained from correlation of features in the UPS spectra, i.e., *d*-band positions and adsorbate emission intensities relative to the Si valence band, with those observed in previous measurements,[11-13] and are only accurate to ~20%. For both Au and Pd on Si(111) (as well as Ag on GaAs[8]), we find an abrupt onset to conduction starting after ~1.5–2 Å of evaporated metal. However, unlike Ag on GaAs,[8] we see no evidence for irreversible stochiometric or structural changes with time or with cooling the sample, *provided* that we start with films evaporated at room temperature.

We have found that given our experimental conditions, there is a unique condition which allows a no-parameter test of this theory. Namely, the function $h(\tau)$ has a maximum for $\beta\tau = 0.56$[10] and since both β and τ can vary with the film thickness d, it is in general possible to vary d until h (and thus the full width at half maximum) obtains its largest possible value. Such maximum broadening is found to occur for an 8.5-Å-thick Au film. The solid line in Fig. 1(a) shows the theoretically calculated temperature dependence of the FWHM, for $\beta\tau = 0.56$, while the circles are the experimental results for this film. Here, our assumption of a largely temperature-independent $\beta\tau$ works well and the temperature-dependent broadening we observe is due to the dependence of Γ on temperature, which arises from the Bose-Einstein factors in the inelastic scattering probability formula. With use of the Boltzmann transport equations (in the relaxation-time approximation), the resistivity ρ is

$$\rho = d/(\epsilon+1)\beta\epsilon_0 v\tau \tag{2}$$

(in SI units), where ϵ_0 is the dielectric constant of vacuum, v is the velocity of the incident electron, and d is the film thickness. Using this known value of $\beta\tau$ and a film thickness corresponding to a uniform metallic layer, gives $\rho \simeq 660$ μΩ cm. In contrast, a Au crystal at room temperature has the resistivity $\rho \simeq 2$ μΩ cm.[14] This thin-film resistivity is too large to be accounted for by surface scattering effects in a uniform Au film but would be consistent with the occurrence of an amorphous gold-Si alloy or silicide, as discussed later. From atomic hydrogen adsorption (i.e., titration) studies on these films,[10] we find no evidence for discontinuous or island films (or the presence of exposed Si surface atoms) above 2.7 Å of deposited Au.

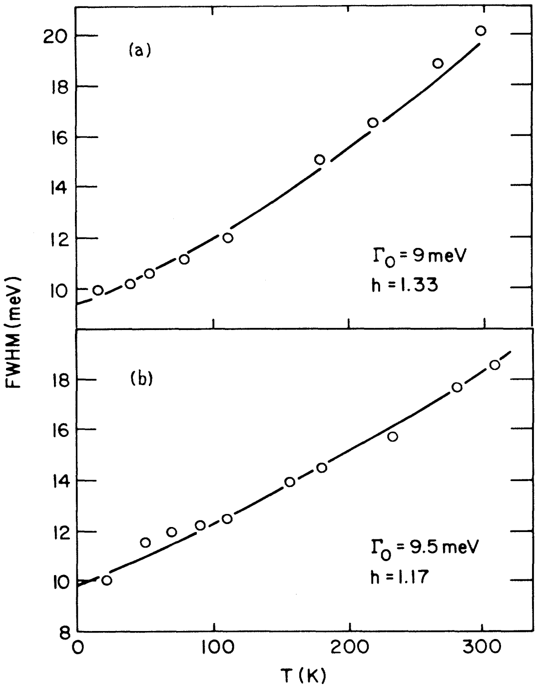

FIG. 1. The temperature dependence of the peak width (FWHM) of the quasielastic peak for (a) 8.5 Å of evaporated Au on top of Si(111) and (b) 10 Å of evaporated Pd on Si(111). The circles are the experimental data and the solid line is the result of a theoretical calculation with (a) $h = 1.33$ and $\Gamma_0 = 9$ meV and (b) $h = 1.17$ and $\Gamma_0 = 9.5$ meV.

After having tested the theory successfully for the Au film we consider the more interesting case of Pd evaporated on Si(111). It is known[12] that Pd evaporated in suffficient quantities on Si(111) at room temperature will react to form a uniform layer of Pd_2Si. Our results for a Pd_2Si film of thickness $\simeq 14$ Å, obtained by evaporation of 10 Å of Pd and annealing to 470 K, are shown in Fig. 1(b). Again, atomic hydrogen titration indicates continuous films, in accord with previous results.[12,15] The FWHM of this Pd_2Si film above ~ 100 K is well described by use of a temperature-independent conductivity with $\beta\tau \simeq 1.11$, which corresponds to a film resistivity of $\rho \simeq 550\ \mu\Omega$ cm. In comparison, a Pd_2Si crystal at room temperature has $\rho \simeq 25\ \mu\Omega$ cm.[5]

An important contribution to the large film resistivity of our ultrathin films is the diffuse scattering at the surface of the film, and a free-electron model for this process predicts[16] that

$$\rho(\text{film}) \simeq \rho(\text{bulk}) \frac{4/3}{(d/l)\ln(l/d)}, \quad d/l << 1, \qquad (3)$$

where l is the mean free path in the bulk. With use of the mean free path of 200 Å found in other thick-film Pd_2Si studies,[5] one obtains $\rho(\text{film}) \simeq 200\ \mu\Omega$ cm for totally diffusive scattering. The slightly larger resistivity that we determine for Pd on Si may indicate greater disorder in our ultrathin films than in the thick films,[5] or the tendency toward forming a metallic glass phase which typically has a higher resistivity, i.e., $\rho(\text{bulk}) \sim 80\ \mu\Omega$ cm.[17] Indeed disorder is suggested since either Au or Pd evaporated on Si(111) attenuates the 1×1 LEED pattern and produces high elastic backgrounds. However, given the simplicity of the above surface scattering model such small differences for Pd on Si may not be meaningful. On the other hand, the surface-scattering contribution for an 8.5-Å pure Au film on Si would give 30 $\mu\Omega$ cm, which is so low that we must conclude that our Au-on-Si film consists of an intrinsically higher-resistivity material. Previous studies suggesting that Au on Si forms an amorphous Au-Si alloy[18] are consistent with our observed resistivity since $\rho(\text{bulk})$ for such alloys is ~ 50–$200\ \mu\Omega$ cm.[19] Furthermore, the abrupt onset to conduction with coverage, which we mentioned earlier, also argues that the high resistivities of both Au- and Pd-derived films are due to a "metallic layer" and not from a surface doping effect of these metal atoms in Si. We also note that we observe some preparation-dependent variations in surface resistivities for both films.

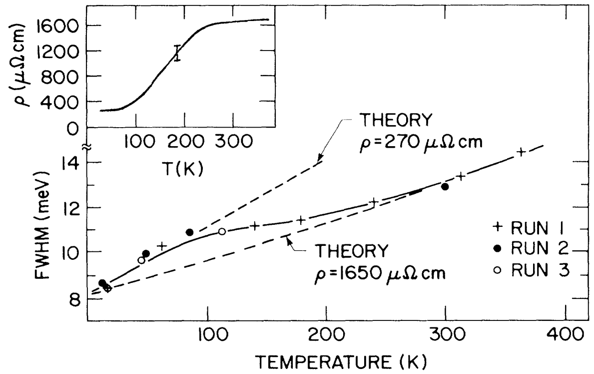

FIG. 2. The temperature dependence of the peak width for 2.5 Å of evaporated Pd on Si(111). The dashed lines indicate a temperature-independent conductivity component determined at higher temperatures and at low temperatures. The inset shows the temperature-dependent resistivity characteristic of this metallic surface layer. (We note that the percolation threshold is found at 1.8 Å of evaporated Pd.)

The electron scattering from all the Pd films that we have studied shows an additional narrowing in the FWHM below ~ 100 K which is not observed in any of our Au films. This feature corresponds to a decreased resistivity at low temperatures and is most obvious at low-Pd coverages where the room-temperature resistivity is much higher, as shown in Fig. 2. Since no such conductivity changes are observed for thick ($\gtrsim 250$ Å) Pd_2Si films,[5] we attribute this feature to some property derived from the surface of the film or the Pd-Si interface compound. We can estimate a temperature-dependent resistivity of this phase by determining its variations from the *constant* resistivity of $\sim 1650\ \mu\Omega$ cm observed at higher temperatures (dashed line) and using the relation between h (which now varies with temperature) and $\beta\tau$. This gives rise to the temperature-dependent conductivity shown in the inset of Fig. 2 which we again note is totally reversible over this temperature range. Here the detailed values and functional dependence of $\rho(T)$ are uncertain because of the small broadening of the elastic beam at low temperatures (an inherent limitation of this approach) and, at higher temperatures, the uncertainties in the assumption of a constant ρ. The absence of such a temperature-dependent conductivity for hydrogen-saturated surfaces, for the Au-covered surfaces, or as a function of specular or diffuse EELS scattering conditions argues that it arises from a physical property of this particular system and is not an artifact of our method.

This derived temperature-dependent resistivity is opposite to that expected from defect-derived variable-range hopping (in the dc limit) or with other localization phenomena. We thus conclude that some other conduction channel associated with the Pd-Si surface or an interface compound arises at low temperatures. We propose that temperature-dependent local stresses at the interface may alter the band structure of the "interface compound" so as to make it more conducting at lower temperatures.

In summary, we present a theory which allows the determination of dc conductivity properties of thin metal layers from EELS measurements and apply this to investigate the properties of ultrathin Au and Pd overlayers on Si(111).

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