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Detection of silicide formation in nanoscale visualization of interface electrostatics

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The ability to detect localized silicide formation at a buried metal semiconductor Schottky interface is demonstrated via nanoscale measurements of the electrostatic barrier. This is accomplished by mapping the Schottky barrier height of the Cr/Si(001) interface by ballistic electron emission microscopy (BEEM). Monte-Carlo modeling is employed to simulate the distributions of barrier heights that include scattering of the electrons that traverse the metal layer and a distribution of electrostatic barriers at the interface. The best agreement between the model and the data is achieved when specifying two barrier heights less than 60 meV from one another instead of a singular barrier. This provides strong evidence that localized silicide formation occurs that would be difficult to observe in averaged BEEM spectra or conventional current voltage measurements. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4979874>]

An electrostatic Schottky barrier at a metal-semiconductor interface is fundamental to many electronic and optoelectronic devices such as source drain contacts in the state of the art FinFET transistors. Low and uniform barrier heights are desired to reduce the parasitic contact resistance, which has been achieved via exotic silicides and monolayer-thick dielectric layers.^{1–6} In the traditional Schottky-Mott model, the barrier height is determined by the work function of the metal and electron affinity of the semiconductor and results from charge transfer from the semiconductor to the metal.^{7–10} At the nanometer size scale, the uniformity of the electrostatic barrier is critical; the absence or presence of a single ionized impurity near the interface, monolayer fluctuations in the dielectric layer, or slight stoichiometry variations in the silicide can significantly alter the electrostatics and resulting performance. Unfortunately, these nanoscale effects are undetectable with the conventional macroscopic current-voltage or capacitance-voltage techniques.

Visualizing the nanoscale fluctuations in the electrostatic barrier at the interface between a metal and a semiconductor is possible with Schottky barrier mapping by ballistic electron emission microscopy (BEEM).^{11–13} BEEM is an STM based technique, where the STM tip is utilized as a local emitter of hot electrons that tunnel into the metal, and the fraction of electrons that make it over the Schottky barrier and into the semiconductor is counted as the BEEM current. BEEM measures the threshold voltage of the unbiased diode, making it the most accurate measure of the barrier height.¹⁴ Schottky barrier mapping is performed by acquiring thousands of BEEM spectra on a grid of tip positions, which are then fit to the Bell and Kaiser (BK) model to extract the local threshold, from which a false-color image of the barrier height can be generated.^{13,15–22} Nanoscale localizations in the electrostatic barrier height are now detectable and when combined with modeling provide a new transformative means to visualize the interface electrostatics.¹³ Improvements in correlating meV shifts in the local barrier height that occur due to incomplete

silicide formation or inclusion of foreign species are needed and will extend the capabilities of the technique.

In this letter, silicide formation is detected at the interface between a metal and a semiconductor through modeling and measuring the electrostatic barrier to nanoscale dimensions. Thousands of BEEM spectra are acquired on a Cr/Si(001) Schottky diode over a square micron and used to generate the map and histograms of the thresholds. Monte Carlo threshold modelling is utilized that includes multiple barrier heights separated by less than 60 meV to achieve a better agreement with the measured data, illuminating the effects of localized silicide formation.

The chromium/silicon Schottky diodes were fabricated by RF magnetron sputtering in a UHV chamber with a base pressure in the 10^{-10} mbar range. A 2 nm chromium layer was deposited on both n- and p- type high resistivity ($10 - 100 \Omega \cdot \text{cm}$) single crystal silicon substrates through a 1×2 mm shadow mask. The doping density of Si is kept constant throughout all BEEM measurements. Prior to deposition, the substrates were cleaned by a standard hydrofluoric acid treatment to remove the native oxide present on the surface. After Cr deposition, the layer was capped *in situ* with an 8 nm Au layer to prevent the possible oxidation of the Cr layer after removal from the UHV chamber. The thickness of the metal layers is confirmed *ex-situ* by ellipsometry, as well as by transmission electron Microscopy (TEM) and energy dispersive x-ray spectroscopy (EDS) for the chemical composition in a FEI Titan S/TEM.

A modified Omicron low temperature, ultra high vacuum (UHV) STM is utilized for BEEM measurements with a base pressure in the 10^{-11} mbar range.²³ The sample is loaded into the UHV environment on a specially designed BEEM plate that allows for independent measurement of the BEEM current, I_B , and tunneling current, I_{tip} . The Ohmic contact, needed for measuring the BEEM current, is achieved by cold-pressing indium between the BEEM plate and the back of the substrate. Two-point IV measurements are taken at room temperature to ensure the rectifying behavior. Then, the sample is cooled to 78 K on the scanning tunneling microscopy (STM) stage

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within 3 h after metal deposition to perform BEEM measurements that are completed within 24 h. Constant tunneling currents of 7 nA for the p-type and 5 nA for the n-type are maintained by the STM feedback loop. A spectrum is collected every 11.7 nm as the tip is rastered over a $1\ \mu\text{m} \times 1\ \mu\text{m}$ area by sweeping the tip voltage from 0.2 V to 2 V for the n-type diodes and $-0.2\ \text{V}$ to $-2\ \text{V}$ for the p-type diodes, which results in 7225 spectra collected during the 24 h period.

A representative spectrum of the sample is generated by averaging all the spectra together. Every spectrum is fit to the simplified BEEM model $I_B = A(V_t - \phi_b)^n$, where V_t is the tip bias, n is the model exponent, A is the amplitude, and ϕ_b is the Schottky barrier height. Each fit is performed by linearizing the BEEM spectra and using a standard linear regression, returning ϕ_b , A , and the quality of the fit parameter, R^2 , where fits with $R^2 < 0.6$ are ignored.²⁴

A Monte-Carlo model is utilized to simulate the histogram of spectra thresholds from individually fit BEEM spectra. The model allows for adjustable inelastic and elastic electron scattering rates Γ_i and Γ_e , respectively, during the electron transport process through the metal base. These values are an empirical account of the scattering being observed in the measurements and are simply an indication of the percentage of spectra with some form of scattering. In addition, ϕ_b and its standard deviation, σ , can also be specified, and a mixture factor for multiple barrier heights is possibly present at the interface. The model simulates the threshold distribution by starting with the same number of measured spectra and then varying the electron energy between 0.2 eV and 2 eV. The scattering

rate is used to randomly scatter a percentage of the simulated electrons elastically or inelastically. Random number generators (mt19937, device_voltage, and taus88 from the BOOST C++ libraries) are utilized. These scattered and un-scattered electrons are compared to a weighted-Gaussian distribution of barrier heights centered around the average measured barrier height. The energy at which the electron's perpendicular momentum is enough to overcome the chosen barrier height is counted as the threshold and added to the distribution.

The average spectra obtained from the BEEM measurements for both p- and n-type substrates are plotted linearly along with their fit and show barrier heights of 0.6 eV (p-type) and 0.59 eV (n-type) in Fig. 1(a) and Fig. 1(b), respectively. Both spectra are plotted together to show that the sum of the barrier heights is equal to 1.19 eV in Fig. 1 which is close to the 1.17 eV gap of Si at 77 K.²⁵ Image force lowering of the barrier heights for these low doped silicon substrates is calculated to reduce the sum by 13 meV.^{24,26} The Cr/Si(001) Schottky diode has been studied with typical I-V and C-V measurements, and the value of 0.60 eV for n-type Si(001) at room temperature has been reported.²⁶ The best agreement with the gap was achieved with the $n = 2$ BK model, and fits to the PK model, $n = 5/2$, were performed but resulted in barrier heights' sum of $\sim 45\ \text{meV}$ less than the bandgap of silicon and lower R^2 values overall. The cross sectional TEM and EDS images of the interface show distinct gold, chromium, and silicon regions with a relatively small region of intermixed chromium and silicon (inset in Fig. 1).

In Fig. 2, the maps of the barrier height show the spatial distribution of the thresholds. The map for the p-type substrate

FIG. 1. (a) Linearized fit of BEEM spectra of the p-type Cr/Si Schottky diode using the exponent of $n=2$. (b) n-type linearized fit of Schottky BEEM spectra. (c) BEEM and BEEM Schottky indicating the summation of the barrier heights. (Inset) (d) Bright field TEM image of the Au/Cr/Si(001) interface and (e) corresponding EDS map.

FIG. 2. Spectra threshold distributions for the (a) p-type and (b) n-type Cr/Si(001) Schottky diodes with associated R^2 values beneath. The inset is the map of the thresholds over a $1\ \mu\text{m}$ squared area. The lines plotted are fits to a lognormal probability distribution function.

shows a high degree of localization with a more disordered interface when compared to the n-type substrate that shows a more uniform barrier height map with only a few localized regions. The histograms of the thresholds from fitting to the individual spectra are plotted in Fig. 2(c) and Fig. 2(d). The n-type histogram has a narrow distribution of spectra thresholds with a peak at 0.59 eV and a small tail to 0.7 eV. In contrast, the p-type histogram has a broader distribution with a peak at -0.6 eV and a high energy tail extending out past -1.0 eV. The skewing of the distributions to higher energy is the origin of the large extrapolation region observed in the fits to the linearized averaged spectra in Fig. 1. This causes the Schottky barrier from the fit to the average spectra to be less than the mean threshold from the distribution as averaging of multiple spectra with different onsets causes the average spectra to deviate from the linearity near the threshold.¹³ However, the fit to the averaged spectra gives the best agreement with the band gap of the substrate and is used as the measured Schottky barrier height.^{13,24}

The skewing of the histograms is an indication of the degree of elastic scattering of the hot electrons, which is displayed more clearly in Fig. 3 and Fig. 4. This has been previously observed and modeled in BEEM measurements of W/Si(001) samples.¹³ The electrons that scatter elastically have their perpendicular momentum reduced, requiring a greater total energy to overcome the barrier. This increase in parallel momentum results in the electrons arriving at the interface without enough perpendicular momentum to surmount the Schottky barrier. This causes the electrons to require a greater total energy to be collected as the BEEM current and skews the distributions to higher tip biases. Another way to describe this is with a maximum or critical angle θ_c for transmission which is dependent on the applied voltage V_{tip} , the Schottky barrier height ϕ_B , and metal Fermi level E_f , which can be written as

$$\theta_c(V_{tip}, \phi_B, E_f) = \sin^{-1} \sqrt{\frac{m_t V_{tip} - \phi_B}{m_e E_f - V_{tip}}}, \quad (1)$$

where m_t is the transverse electron effective mass in the semiconductor ($m_t = 0.19 m_e$ in Si).^{11,27}

The results from the Monte Carlo simulation using one threshold at the interface from the mean of the data are plotted on top of the measured data and displayed in Fig. 3(a) and Fig. 4(a). In addition, R^2 values of 0.92 and 0.96 for the p-type and n-type, respectively, are calculated to quantify the agreement between the model and the data. This was arrived at after an exhaustive search over all possible values of Γ_e , Γ_i , and σ . However, the quality of fit is unable to be increased by simply adjusting these parameters. The model disagrees slightly with the leading edge, peak, and tail of data for both samples. The inability to further increase the quality of fit is an indication that the skewing to higher energies and asymmetry in the distributions are not solely from elastic scattering.

A better agreement is achieved when including an additional threshold ϕ_{b2} , its standard deviation σ_2 , and a relative threshold mixture factor μ of the amount of ϕ_{b1} to ϕ_{b2} at the interface in the model. The first threshold is kept fixed from the single threshold fit, while a comprehensive search over ϕ_{b2} , σ_2 , and μ is performed to maximize the R^2 value. The best agreement is achieved with ϕ_{b2} within a few meV of ϕ_{b1} as summarized in Table I and plotted in Figs. 3(b) and 4(b). The addition of the second threshold increases the R^2 values to 0.99 for the n-type and 0.98 for the p-type and provides a much improved visual agreement between both distributions. Γ_e was decreased in the p-type sample to achieve a better agreement, which brought it closer to the value used in the n-type sample as indicated in Table I. Reducing Γ_e in the n-type sample did not improve the agreement. The slightly larger value of Γ_e for the p-type sample indicates that more elastic scattering occurs in the p-type sample, which is consistent with its greater thickness.

FIG. 3. (a) Cr/n-Si(001) modelled histogram and data showing skewing to higher energies and degree of agreement between the two. (b) Improved agreement when a second threshold is added to the simulation with a mixture factor of 0.9.

The small differences in energy between ϕ_{b1} and ϕ_{b2} are 60 meV for the p-type sample and 10 meV for the n-type sample and are attributed to partial chromium-silicide formation at the interface, which is supported by the slightly intermixed Cr and Si region observed in the TEM images displayed in Fig. 1. Typically, changes in barrier heights due to silicide formation are on the order of tens of meV as has been observed when comparing annealed and nonannealed W/Si measurements.^{13,21,22,28} In contrast, prior Schottky barrier mapping of the miscible Au-Ag/Si diodes displayed much broader threshold distributions with $\sigma \approx 100$ meV and multiple peaks resulting from gold diffusion through the thin silver and the 200 meV difference in barrier heights of the two metals to silicon.²² Gold diffusion through these gold-capped chromium films would result in a much larger ϕ_{b2} since its barrier height to silicon is 0.85 eV (n-type) and -0.31 eV (p-type). In addition, gold and chromium are not soluble with one another and do not form an alloy as readily

FIG. 4. (a) Cr/p-Si(001) modelled histogram and data showing skewing to higher energies and degree of agreement between the two. (b) The improved agreement when a second threshold is added to the simulation with a mixture factor of 0.5 and a reduced Γ_e of 24%.

as gold and silver, and gold is not observed at the silicon interface in the TEM results displayed in Fig. 1.^{22,29} Isolated dopant atoms near the interface are neglected due to the low doping density of the substrates. The mixture factor is a

TABLE I. Values utilized in the modeling of the BEEM threshold distributions displayed in Fig. 3 and Fig. 4.

	p-type			n-type		
	Single ϕ_t	Double ϕ_t	Double ϕ_t	Single ϕ_t	Double ϕ_t	Double ϕ_t
ϕ_t	-0.64	-0.64	-0.64	0.59	0.59	0.59
σ	0.078	0.078	0.078	0.023	0.023	0.023
Γ_e	41%	41%	24%	15%	15%	0%
ϕ_1	-0.61	-0.61	-0.60	0.591	0.591	0.59
σ_1	0.051	0.051	0.029	0.009	0.051	0.009
ϕ_2	...	-0.66	-0.66	...	0.595	0.595
σ_2	...	0.065	0.065	...	0.009	0.009
μ	...	0.5	0.5	...	0.9	0.9
R^2	0.92	0.812	0.983	0.964	0.990	0.948

measure of the relative amount of counts attributed to each barrier height at the interface. It can be taken as a measure of the degree of silicide formation where μ for the p-type is less than that for the n-type. This suggests that more silicide is formed on the p-type sample as displayed in Table I and would be consistent with the thicker Cr layer of the p-type sample and possibly slight variation in processing conditions. Caution should be taken when ascribing the two barrier heights reported from the modeling to a precise measure of the barrier heights for silicide and nonsilicide as pinch off effects tend to compress barrier heights from intermixed metal species.^{9,10,19} This results from the continuity of the electrostatic potential at the interface and is proportional to the physical distribution of the two intermixed species.

Detection of localized silicide formation at a buried metal semiconductor interface via measurement of the electrostatic barrier to nanoscale dimensions and modeling with Monte-Carlo simulation is demonstrated. The best agreement between the model and the data is achieved when specifying two barrier heights within 60 meV of one another, which provides strong evidence that localized silicide formation occurs that would be difficult to observe in averaged BEEM spectra or conventional current voltage measurements.

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