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Monolayers and nanoparticles on nickel silicide for molecular electronics

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We describe the use of nickel silicide as an electrode in molecular electronics applications. Formation of monolayers of aliphatic and aromatic hydrocarbons on nickel silicide is demonstrated, and these monolayers are used to link CdSe nanocrystals to the substrate. Using the conjugated linker molecule 1,4-ethynylphenyl-2'-nitro-1-benzene-dithiolate, scanning tunneling spectroscopy measurements at 120 K show evidence of Coulomb blockade and resonant tunneling behavior associated with the nanocrystals. These measurements demonstrate the feasibility of using nickel silicide as an electrode in molecular electronic devices. © 2006 American Institute of Physics. [DOI: 10.1063/1.2190458]

Electronic devices using organic molecules or inorganic nanoparticles as the active element represent the ultimate in miniaturization, but many challenges remain in interfacing large numbers of these devices to macroscopic circuits.¹ Silicon processing technology provides a well-established method to produce arrays of electrode structures which might be used to contact nanoscale circuit elements.² However, the silicon surface forms a native oxide which acts as a barrier to electron transport, and which makes it difficult to assemble molecules in such a way that they are in direct electrical contact with the underlying semiconductor. By converting the top layer of the silicon into a metal silicide, it is possible to provide a stable, conducting surface which can be used as an electrode.³ This silicidation process is used to form gate and interconnect structures in current silicon-based microelectronic devices. In this letter, we show that monolayers of thiolated molecules can be formed on nickel silicide surfaces. These monolayers are used to attach CdSe nanocrystals to the surface, and the electrical properties of the resulting films are investigated using scanning tunneling spectroscopy (STS).

Nickel disilicide samples were obtained by thermal evaporation of 50 nm Ni on boron-doped Si (100) substrates with a conductivity of $1-10 \Omega$ cm, followed by rapid thermal annealing at 800 °C for 3 min under a nitrogen atmosphere. The thickness of the silicide layer was estimated to be 180 nm. The samples were dipped in buffered hydrofluoric acid to remove any surface oxides, and rinsed in deionized water. The conjugated phenyleneethynylene oligomer 1,4-ethynylphenyl-4'-ethynylphenyl-2'-nitro-1-benzene-dithiolate (EP2NO₂) was chosen for assembly on the surface since its monolayers are known to exhibit interesting nonlinear properties in molecular electronic devices.^{4,5} EP2NO₂ was synthesized using literature procedures,^{6,7} and

its structure is shown in the inset of Fig. 2. The substrates were immersed in a solution containing 0.1 mM of the thioacetate derivative of EP2NO₂ in tetrahydrofuran (THF) and 500:1 aqueous ammonia (volume/volume) for 24 h, followed by thorough rinsing with THF. For comparison, the insulating aliphatic molecule 1,6-hexanedithiol was also assembled on a separate substrate. CdSe nanocrystals of diameter \sim 4 nm were synthesized by standard methods^{8,9} and assembled onto the exposed thiol surface by immersing the substrates in a toluene solution containing 0.016 wt % of nanocrystals coated by trioctylphosphine oxide for 24 h, followed by thorough rinsing. Similar strategies for assembly of CdSe nanocrystals have previously been demonstrated on both metallic¹⁰ and semiconducting¹¹ surfaces.

Attenuated total internal reflection Fourier transform infrared spectroscopy (ATR-FTIR) measurements showed peaks at 2854 and/or 2925 cm⁻¹ corresponding to the CH stretching vibrations of the aliphatic and aromatic hydrocarbons, respectively. This confirms the presence of the organic molecules on the surface, and the shifts in these peaks compared with the bulk values suggest that the molecules are closely packed.^{12,13} Photoluminescence peaking at 601 nm was observed under excitation at 488 nm, confirming the assembly of CdSe nanocrystals on the surface. The emission spectrum was identical to that of the nanocrystals in solution. No luminescence was observed in control samples processed in the same way but using 1-dodecanethiol. Infrared and photoluminescence spectra are provided as supplementary material.¹⁴ In order to assess coverage, contact angles for sessile water droplets were measured for various organic monolayers on nickel. 1-dodecanethiol gave a contact angle of 99°, less than the value of 110° obtained for self-assembled monolayers on gold,¹⁵ but significantly more than the 68° obtained on the nickel silicide substrate. This indicates that the layers do not have the well-ordered structure obtained on gold, but nevertheless the coverage is substantial. For EP2NO₂ the contact angle of 76° is again signifi-

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FIG. 1. Scanning tunneling spectroscopy measurements at 120 K for 1,6hexanedithiol monolayers on nickel silicide at 120 K. Data are shown for the nickel silicide substrate only (labeled with occasional squares), with 1,6-hexanedithiol (diamonds), and with 1,6-hexanedithiol and CdSe nanocrystals (circles). Spectra are averaged over 25 scans from negative to positive bias at different places on the sample.

cantly larger than that of the substrate, and is consistent with the presence of a thiol group at the film surface, which is expected to give more polar behavior than 1-dodecanethiol.¹⁰ Further work is necessary to determine the degree of packing, ordering, and orientation in the organic monolayers, but these results indicate that the monolayers are reasonably dense and well packed.

Ultrahigh vacuum STS measurements were obtained at 120 K in an Omicron variable-temperature UHV scanning probe microscope using platinum-iridium scanning tunneling microscopy (STM) tips (Materials Analytical Services, radius approximately 50 nm). Current-voltage characteristics were obtained by sweeping the applied voltage between ±2.5 V at a rate of 500 V/s. STM measurements were performed at a tunneling current of 0.1 nA. STS measurements were performed at a fixed tip height, set to give a tunneling current of 0.2 nA at -2 V. Similar parameters were previously used by Walzer et al.¹⁶ to study the current-voltage characteristic of self-assembled monolayers of CdSe nanocrystals on GaAs surfaces. Current-voltage characteristics were averaged over 25 scans at different points on the sample from negative to positive bias unless stated otherwise.

Figure 1 shows the STS spectra of 1,6-hexanedithiol monolayers on nickel silicide. The spectra for the bare substrate and for the organic monolayer are largely symmetric about zero bias, show no obvious conductivity gap, and are consistent with the behavior expected for a metallic substrate separated from the tip by a dielectric gap. The addition of a layer of CdSe nanocrystals gives a slight increase in current at small biases, but does not significantly affect the shape of the current-voltage characteristic. Surprisingly, no additional features associated with Coulomb blockade or resonant tunneling are observed.

Figure 2 shows the STS spectra of samples using EP2NO₂ as the linker layer. Addition of the EP2NO₂ layer alone gives increased current at low voltages compared with the substrate and with the hexane-dithiol layer. Addition of CdSe nanocrystals gives a significant change in the form of the current-voltage characteristic, with a clear conductance gap around zero bias, and an asymmetry between forward and reverse bias. The differential conductance shows a clear peak centered around -1.3 V, which is attributed to the reso-



FIG. 2. Current-voltage characteristics at 120 K for a monolayer of 1,4ethynylphenyl-2'-nitro-1-benzene-dithiolate (EP2NO₂) on nickel silicide (triangles), and for the same monolayer with CdSe nanocrystals (circles). The differential conductance of the latter sample (squares) is also shown. Spectra are averaged over 25 scans from negative to positive bias at different places on the sample. The inset shows the structure of EP2NO₂.

nant tunneling of holes from the tip to the occupied molecular orbitals of the nanocrystals. There is also some evidence of a peak around +1.4 V, which is attributed to resonant tunneling of electrons from the tip to the unoccupied molecular orbitals of the nanocrystals. STS of CdSe nanocrystals separated from a metallic substrate by an insulating monolayer has been studied in detail by Bakkers *et al.*¹⁷ Comparison with their results suggests that the sample is in the "shell tunneling" regime, where the tunneling of charges from the nanocrystals to the substrate is much faster than the tunneling of charges from the tip onto the nanocrystal. Although the set point for our measurement implies a smaller tipnanocrystal distance than was used by Bakkers et al., since we use a conjugated monolayer the tunneling rate from nanocrystal to substrate is likely to be enhanced, consistent with working in the shell tunneling regime. Enhanced tunneling is expected due to the presence of relatively low-lying highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels in EP2NO₂. We note that there is also the possibility for the charge to become localized on the EP2NO₂ molecule, leading to a more complex three-step tunneling process.

The STS spectra presented so far have been averaged over 25 scans at different points on the sample. More detailed information about the tunneling process can be obtained by examining individual current-voltage scans for both positive and negative scan directions, as shown in Fig. 3. Peaks in the conductance spectrum are now much clearer, since the effects of inhomogeneous broadening due to the nanocrystal size distribution and the differences in coupling to the organic monolayer are no longer important. When the voltage is swept from positive to negative, a sharp peak at -1.55 V is seen. This peak is significantly broadened when sweeping from negative to positive. Conversely, the peaks in forward bias are more prominent when sweeping from negative to positive. These hysteresis effects are likely to be due to rearrangements in the local structure of the monolayer,¹⁸ or in the coupling of the nanocrystals to the monolayer. Cou-

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FIG. 3. Individual current-voltage characteristics at 120 K for CdSe nanocrystals on $EP2NO_2$ on nickel silicide (circles). Differential conductance is also shown (squares). Solid and broken lines represent scanning from positive to negative and negative to positive bias, respectively.

plings to torsions within the EP2NO₂ (Ref. 19) and the effect of charge localization in the monolayer²⁰ may both play a role in producing the observed hysteresis.

Our results show that nickel silicide is suitable for use as an electrode in molecular electronic devices. Monolayers of both aliphatic and aromatic molecules can be deposited on its surface, and STS measurements demonstrate electrical contact of the molecules to the substrate. Using CdSe nanocrystals attached to the silicide substrate by aromatic monolayers we see evidence of Coulomb blockade and resonant tunneling effects. These results demonstrate that silicidation provides a possible route for making contacts to molecular electronic devices from silicon-based circuits.

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