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Electroluminescence from Nanocrystals in an Electromigrated Gap Composed of Two Different Metals

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ABSTRACT

We present a technique for making nanoscale gaps with work function offsets based on electromigrating leads composed of two different metals. Electroluminescence spectra from plain metal gaps with and without CdSe/ZnS (core/shell) nanocrystals are qualitatively very similar and exhibit features that are much broader than the photoluminescence spectra obtained from the same nanocrystals. These observations can be explained by inelastic scattering of conduction electrons in the metal leads or by electroluminescence from small metallic clusters that can form during the fabrication process. However, electroluminescence that spectrally coincides with nanocrystal photoluminescence can be observed in devices containing nanocrystals formed by electromigrating Pt leads bridged with small indium islands. This suggests that electromigrating leads made of different metals is a promising route to fabricating nanoscale gaps with work function offsets for optoelectronic devices.

Over the last years, nanoscale optoelectronic devices have become of significant scientific and practical interest.[1–6] Smaller device dimensions not only allow for higher packing density, but can also help elucidate the optoelectronic processes, information that is useful for designing more efficient macroscopic nanocrystal-based light emitting diodes (LEDs)[7,8] and solar cells.[9] Nanoscale light sources could also find applications in spacially resolved sensing and as tips in scanning near field optical microscopy.

A central challenge toward achieving nanoscale light sources is to identify suitable fabrication techniques and materials. Semiconductor nanowires are very promising candidates.[2,10,11] Semiconductor nanocrystal quantum dots lead to an even stronger reduction in size and allow for the emission wavelength to be tuned continuously over the entire visible range by varying the nanocrystal diameter.[12,13] Single nanocrystal electroluminescence (EL) has previously been observed in organic LED structures[6] and in inorganic devices fabricated by molecular beam epitaxy,[1,3,5,14] as well as in planar transistor geometries.[4] Planar transistor geometries are better suited for realizing complex circuits and integration with existing silicon technology. Electroluminescence spectra reported from single CdSe nanocrystals in planar devices, however, are very broad and do not coincide with nanocrystal photoluminescence (PL) spectra due to inelastic scattering in the metal leads.[4]

Using leads made of two different metals with suitable work functions should help achieve ambipolar operation and, hence, reduced emission from inelastic scattering. Previous studies have employed e-beam lithography[15] and electrochemical techniques[16] to fabricate electrodes made of two different metals with nanometer separation. Gaps formed by electromigration have the advantage of being very clean, because they can be opened in situ in vacuum and under cryogenic conditions with only the molecules or nanoparticles present that are intended to bridge the gap.[17,18] This is of particular interest when low work function metals are employed, because they tend to be unstable under ambient conditions. Here, we investigate how the advantages of electromigrated gaps can be extended to include work function offsets.

Samples were fabricated using degenerately doped silicon substrates covered with a 300 nm thick layer of insulating thermal silicon oxide. Macroscopic contact pads were prepared by optical lithography, and metal bridges of gold or platinum with a thickness of 50 nm and a width of 100−200 nm were subsequently defined by e-beam lithography. The samples were rinsed in acetone and 2-propanol and descummed in an oxygen plasma asher for 3 min, before being mounted in an optical cryostat.

Electromigration was performed in vacuum at a base temperature of approximately 10 K. A scanning electron microscope (SEM) image of a typical gap formed in a gold bridge is shown in Figure 1b. The resistance trace shown in

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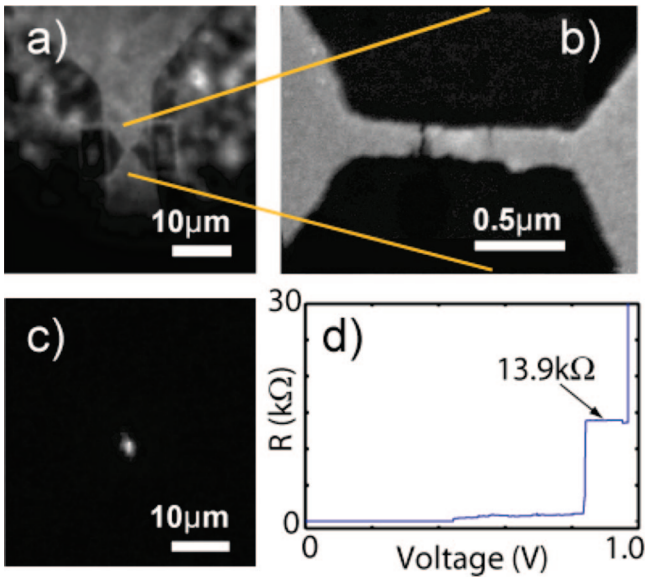

Figure 1. (a) Microscope image of a device mounted in an optical cryostat under laser illumination. Dark features are gold contacts and the bright background is the fluorescing layer of nanocrystals. (b) Scanning electron microscope image of an electromigrated gold bridge (bright). (c) Same image as in (a) with the laser blocked and the device electroluminescing. (d) Resistance as a function of bias during the electromigration process for a plain gold bridge.

Figure 1d was obtained by ramping up the voltage at a rate of 1 mV/s.

Weak illumination with the 514 nm line of an Ar ion laser was used to image and focus on the gap region (Figure 1a). Then the laser was blocked, and the EL was recorded as a function of bias with an intensified CCD camera (Figure 1c). Corresponding EL spectra as a function of bias from an electromigrated gold gap are shown in Figure 2a. Similar spectra were obtained when CdSe/ZnS core/shell nanocrystals with photoluminescence peaks centered around 650 nm were dropcast before or after electromigration (Figure 3a). (CdSe/ZnS nanocrystals were either synthesized using standard techniques[19,20] or accquired from Quantum Dot Corp.) The samples presented in Figures 2a and 3a were particularly stable compared to other devices. In all samples where EL was present, we observed broad features roughly between 600 and 800 nm, sometimes exhibiting multiple peaks, regardless of whether nanocrystals were present or not. We measured more than 10 of these types of samples including samples made by electromigrating platinum bridges, and all showed qualitatively very similar features.

For the In/Pt bimetal samples, 1 μm wide platinum leads with a gap width of 100 nm and a thickness of 50 nm were fabricated by e-beam lithography. The samples were rinsed in acetone and 2-propanol and descummed in an oxygen plasma asher for 3 min, before a thin layer of indium was evaporated through a shadow mask over the entire gap area. As shown in Figure 4a−d, thin indium films break up into small islands during the evaporation process. This makes thin indium films electrically insulating on a micrometer scale. The diameter of the indium islands can be tuned by the layer thickness, which makes it possible to control the degree of bridging of the indium islands across the 100 nm wide gap

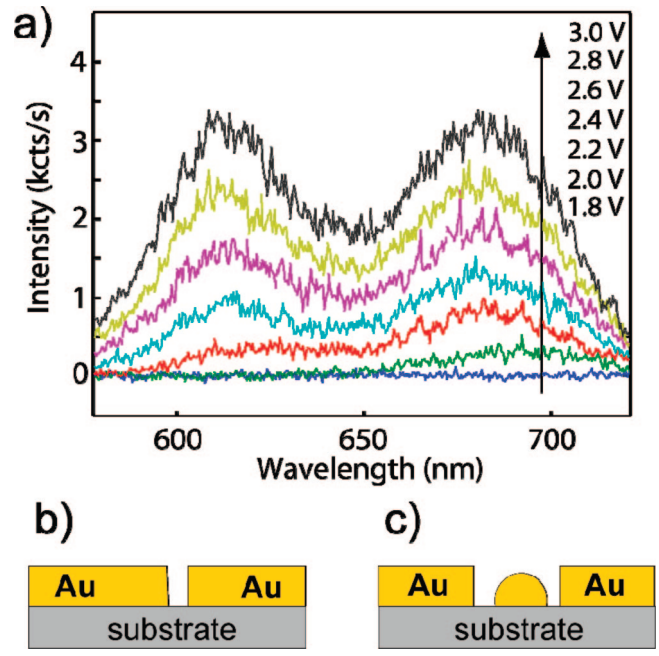

Figure 2. (a) Electroluminescence spectra at a series of bias voltages for a plain electromigrated gold gap at 10 K. (b) and (c) Schematics illustrating possible configurations of the electromigrated gap.

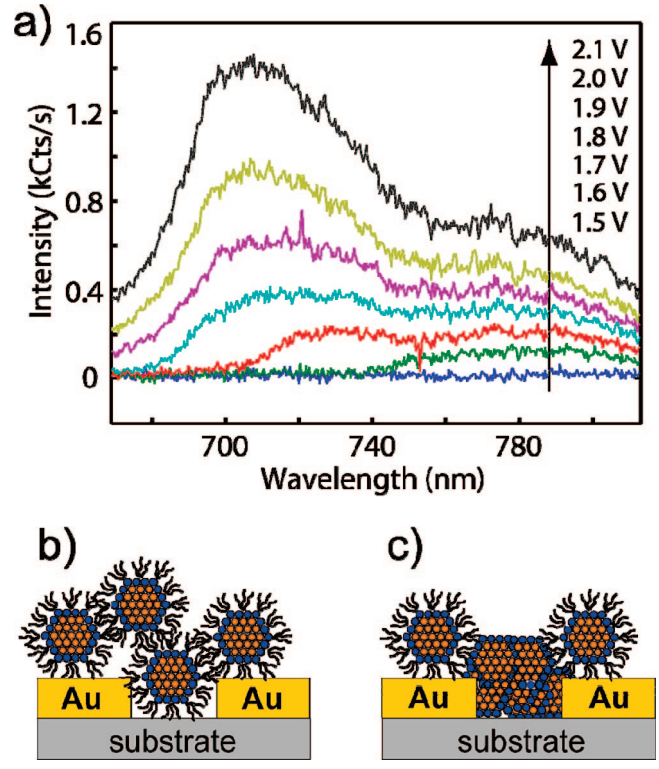

Figure 3. (a) Electroluminescence spectra at a series of bias voltages for a gold gap that was electromigrated at 10 K after dropcasting nanocrystals. The nanocrystals could bridge the gap as illustrated in (b) or could be sintered and fused onto the leads by the heat of electromigration as depicted in (c).

between the platinum electrodes. A 50 nm thick indium film leads to an island diameter of about 190 ± 30 nm (Figure 4a), which is considerably larger than the ∼100 nm gap between the platinum electrodes. Islands of this size that bridge the gap can heat up during electromigration and form

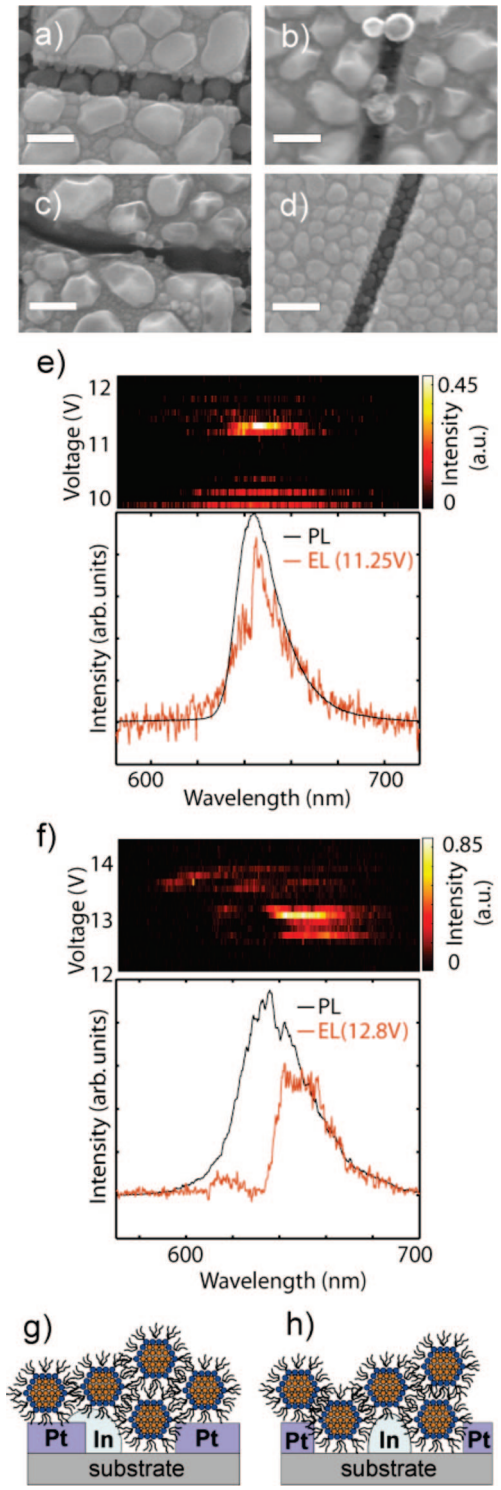

Figure 4. (a) Scanning electron microscope image of a 100 nm wide platinum gap covered with a 50 nm thick indium film that has broken up into islands. During electromigration the indium can melt and is drawn into the gap by electrostatic forces (b). At even higher biases, the gap will "burn" open (c). If only 20 nm of indium is deposited, smaller islands form and there is no visible difference after electromigration at the resolution of our SEM (d). In all images the scale bar corresponds to 250 nm. The upper panels in (e) and (f) are color plots of bias-dependent EL spectra of two devices as shown in (d) covered with nanocrystals. The lower graphs compare the EL spectra at a given bias with PL spectra taken at the same position on the devices, all at 10 K. (g) and (h) Possible configurations of In/Pt gaps covered with nanocrystals.

liquid droplets that can persist up to very high temperatures leading to significant thermal stress before the gap opens (Figure 4c). This can be prevented by using a 20 nm indium film that forms islands with diameters of about 80 ± 20 nm, which is close to the gap width of the platinum electrodes. In this case, the samples before and after electromigration were indistinguishable in our SEM with a resolution of about 5 nm (Figure 4d). The resistance of the indium-covered platinum gaps varied widely because of random configurations of indium islands in the gap. Nanocrystals were dropcasted as described above for the plain metal samples, before electromigration was performed. The resulting nanocrystal layers had a thickness of 20–100 nm and tended to be inhomogeneous owing to the metal electrodes. An alternative method was to soak the samples in a solution with 5 mM 1,6-hexanedithiol in ethanol for more than 24 h and then to immerse them in a hexane/nanocrystal solution for approximately 12 h. Electroluminescence spectra as a function of bias for devices fabricated by the first and second method are shown in panels e and f of Figure 4, respectively. Of the nine devices measured, five showed EL that coincided with nanocrystal PL, two exhibited broad, nonspecific spectra, and two were insulating.

In the plain metal samples, EL can arise from different configurations. As shown in Figure 2b, direct tunneling across a small gap can lead to light emission as observed in scanning tunneling microscopes, where tunneling electrons can trigger plasmons in the probe tip and/or substrate.[21–23] Small metal clusters can also be present in electromigrated gaps (Figure 2c) and lead to EL as described by Gonzalez et al.[24] Multiple peaks can arise from several metal clusters being excited simultaneously. The spectral features observed in our measurements (Figure 2a) are consistent with these earlier reports. High energy dissipation in the gap leads to continued electromigration during operation and limits the stability of the devices. As a result, strong fluctuations in EL intensity and spectra were often observed and some contributions from blackbody radiation could sometimes be present.[25]

A schematic of an electromigrated gap covered with nanocrystals is shown in Figure 3b. If the nanocrystals are deposited before electromigration, it is possible that some of the nanocrystals sinter and fuse onto the leads as illustrated in Figure 3c. Electroluminescence spectra from devices where nanocrystals were deposited before or after electromigration were very similar and comparable to those observed in plain metal samples and as reported for single CdSe nanocrystal transistors.[4] This confirms that EL in these types of samples is dominated by inelastic scattering and plasmon modes in the metal leads and/or metal clusters rather than by radiative recombination of excitons in the semiconductor nanocrystals. The main reason for this is probably asymmetric coupling and pinning of both leads to either the valence or conduction bands of the nanocrystals.[4,26]

In order to overcome this problem, we fabricated gaps containing indium and platinum as described above, which have a work function offset of 1.53 eV[27] (Figure 5). This should facilitated hole injection into the nanocrystals from

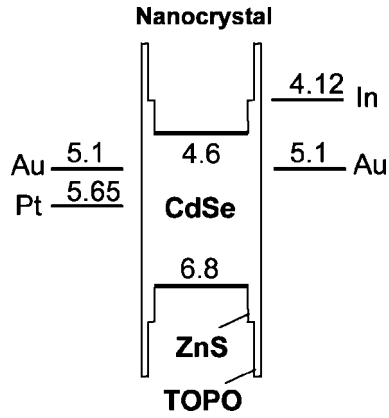

Figure 5. Work functions of gold, platinum, and indium[27] relative to the valence and conduction band levels of a CdSe/ZnS nanocrystal.[28]

the platinum contacts and electron injection from the indium contacts.[26,28] An additional advantage of using indium is that it has plasmonic features to the blue of the nanocrystal emission[29,30] which prevents exciton energy transferring from the nanocrystals to the indium plasmons. These devices are capable of emitting EL that spectrally coincides with PL of the nanocrystals (panels e and f of Figure 4). A schematic of an ideal configuration for ambipolar operation is shown in Figure 4g.

Single, isolated, nanocrystals of the type used for our devices typically have PL spectral widths <1 nm at a temperature of 10 K. The larger PL peak widths of films of nanocrystals (FWHM, 20–30 nm at 10 K) are due to ensemble broadening arising from small variations in nanocrystal size as well as spectral diffusion. It should also be noted that PL spectra of films of nanocrystals are dominated by the larger nanocrystals, because excitons in smaller nanocrystals tend to undergo Förster energy transfer to larger nanocrystals in their vicinity before radiatively recombining. In EL, the very small gap widths as shown in Figure 4a−d, together with the fact that tunneling is extremely sensitive to small differences in nanocrystal/lead coupling, heavily favors conduction through the point of strongest coupling as in a scanning tunneling microscope. It is therefore probable that only a few nanocrystals are electrically active. The blue sides of EL spectra are dominated by the smallest nanocrystals being electrically excited and can be expected to show sharp rises typical of single nanocrystal PL peaks. As in PL from nanocrystal films, subsequent Förster energy transfer to larger nanocrystals close to the electrically active nanocrystals will result in long tails to the red that coincide with the ensemble PL spectra. Therefore, the EL spectra in panels e and f of Figure 4 were scaled to match the PL spectra at wavelengths longer than 660 nm. In this region the red tails of the EL and PL spectra coincide. The shapes of the complete EL and PL spectra, however, are qualitatively different from each other. In Figure 4e the peak rising out of the EL spectrum around 650 nm is significantly sharper than the ensemble PL peak, indicating that only a small number of nanocrystals are being preferentially electrically excited. Interestingly, the EL spectrum at 12.8 V in Figure 4f exhibits two peaks, a small one centered around 620 nm and a larger one centered around 650 nm, that are enveloped by the PL spectrum taken at the same position. The sharp rise on the blue side of the large EL peak in Figure 4f is consistent with a small number of electrically active nanocrystals. The long tail to the red coincides with the ensemble PL spectrum and may be caused by spectral diffusion and/or Förster energy transfer to larger nanocrystals close to the nanocrystals active in EL, as discussed above.

In contrast to samples containing only one kind of metal, EL in the In/Pt samples was typically observed at voltages significantly higher than the corresponding energy of the emitted photons. This could be a result of configurations as depicted in Figure 4h, where two or more platinum/nanocrystal/indium junctions are connected in series with opposite polarity, one in reverse bias and the other in forward bias. A configuration with platinum/nanocrystal/indium/gap/platinum is also possible. These configurations are likely since indium does not easily wet platinum, as appears to be the case from the SEM images in Figure 4a−d. In either of these configurations most of the voltage drops over the tunneling gap or junction that is in reverse bias, while the nanocrystals in forward bias luminesce. These configurations strongly reduce device efficiency and require higher operating voltages, but still maintain the device's ability to emit EL that spectrally coincides with nanocrystal PL. Another possibility is that tunneling between indium islands could trigger plasmons to the blue of the nanocrystal PL, which would subsequently excite nearby nanocrystals by energy transfer. However, we were not able to observe any emission to the blue of the nanocrystal PL in any devices, including those without nanocrystals.

In conclusion, we have shown that electromigrating junctions containing two metals with different melting points and work functions can be used to fabricate nanoscale optoelectronic devices that exhibit electroluminescence, which spectrally coincides with the photoluminescence of the material in the gap. In contrast, gaps formed by electromigrating only one metal show broad electroluminescence spectra originating from inelastic scattering, as has been reported previously. In addition, electromigrating gaps containing indium places less thermal stress on the particles intended to bridge the gap than if noble metals are used. This could be of particular interest when heat-sensitive particles or molecules are present. The technique of bimetallic electromigration presented here should be extendable to many other combinations of metals, thus opening a promising route to fabricating a wide range of nanoscale optoelectronic devices.

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