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Colloidal Au/Linker Molecule Multilayer Films: Low-Temperature Thermal Coalescence and Resistance Changes

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A decrease in the resistance of colloidal Au multilayer films, fabricated by the layer-by-layer assembly process on flexible polymer substrates, was observed upon heating. This decrease occurs because of the oxidation and desorption of the linker molecules from the film, leading to a coalescence of the Au particles, thus forming more conducting pathways. Three linker molecules: 2-mercaptoethanol (ME), 1,6-hexanedithiol (HD), and 1,10-decanedithiol (DD), having different lengths, were chosen for the fabrication of the films. The initial resistance of the films was considerably different for the three linker molecules, 50 Ω, 1 MΩ, and >100 MΩ, respectively. The films were heated at three different temperatures: 120, 160, and 180 °C. The resistance of the films was found to be a strong function of the time and temperature of heating. After heating for sufficiently long times or at higher temperatures, the resistance of the ME film decreased to 5 Ω and to about 50 Ω for the HD and DD films. The lowest resistivity obtained, 6×10^{-5} Ω·cm, was about 25 times that of bulk gold. The films were characterized by UV−vis spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, and atomic force microscopy.

Introduction

Films fabricated by the self-assembly of colloidal particles have been a topic of many recent research efforts, mainly because of the ability to control and tune the physical and chemical properties at the nanometer level.[1−10] The colloidal particle films that have generated the greatest interest have been fabricated from Au and Ag colloids. These films have been used in a wide variety of applications that include their use as substrates for surface-enhanced Raman spectroscopy (SERS)[11−13] and surface plasmon resonance (SPR),[14,15] as surfaces for the immobilization of redox-active species,[16] as electrode materials,[17] and as chemiresistors used in vapor sensing.[18,19] Self-assembly of Au and Ag films from colloidal solutions onto glass or silicon substrates has been demonstrated previously by many groups.[20−22] The formation of a Au or Ag monolayer on the surface is achieved by the immobilization of the particles on functionalized surfaces containing groups such as $-NH_2$, $-SH$, and $-CN$ that have an affinity for the particles.[10,23] These particles are tightly bound to the surface and do not desorb in solution. Varying the surface coverage can lead to interesting optical and electronic properties. This can be achieved in a number of ways such as changing the size of the colloidal particles,[15,24] reduction of Au onto the attached monolayer (seeding approach),[25,26] or formation of multilayers using organic linker molecules.

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Apart from controlling the size of particles and coverage, the use of linker molecules provides another parameter that can be used to tune the film properties. These films can be fabricated either using the layer-by-layer (LBL) assembly of the Au colloid and the linker molecule[20b,21b] or by using Au colloids stabilized with organic molecules (monolayer-protected clusters, MPCs).[22] The optical and electronic properties of these films can also be tuned by changing the structure or molecular weight of the organic molecules.[27,28] The LBL assembly of Au colloids involves the alternate immersion of a functionalized substrate into the colloidal Au solution and a bifunctional organic molecule solution. Bethell et al.[20a] have fabricated films using Au colloids and have observed that the electrical conductivity of the films was a function of the length of the linker molecules and decreased as the length of the linker molecule increased. Similar results were obtained by Musick et al.[29] They reported that, upon using a small cross linker with a 2-C chain, the resistivity of a 12-layer film of 11-nm Au particles was about 5×10^{-4} Ω·cm, whereas it was as high as 3.6×10^{8} Ω·cm for a film fabricated from 2.4-nm Au particles using a 16-C chain molecule.

Liu et al.[30] have fabricated multilayer films by the alternate immersion of glass substrates in a solution of Au particles coated with a cationic polymer followed by an anionic polymer. These films fabricated by the electrostatic self-assembly method had resistivities of 5×10^{-6} Ω·cm. Other studies have described the electron-transport properties in these multilayer films indicating an electron-hopping mechanism for charge transport,[20b] the electrochemical properties of the Au multilayer electrode with respect to various redox probes,[31,32] and optical properties of dithiol linked Au multilayer films.[33] Au multilayer films can also be fabricated using Au particles stabilized with organic molecules or MPCs. Joseph et al.[19] have used dodecylamine-stabilized Au nanoparticles and different dithiol molecules to fabricate films by the LBL approach and have described the charge transport and vapor sensing properties. Murray and coworkers performed a number of studies on MPCs of Au nanoparticles stabilized by different ligands. Metal films were fabricated by LBL attachment of the MPCs,[34] drop casting, or painting onto glass substrates, and subsequent thermal annealing at temperatures of about 300 °C gave conductive metal films.[22a]

Most of the previous work on self-assembled Au films has been done on rigid substrates such as glass or silicon. In a previous report we have described the fabrication of conductive Au films on flexible polymeric substrates using a solution-based seeding approach.[35] This paper describes the fabrication of multilayer Au films by the LBL approach using three different dithiol molecules on flexible polymeric substrates. The electrical properties of the films have been investigated as a function of the length of the linker molecules, and similar to observations made in previous reports, the resistivity was found to increase with the increase in the length of the linker. Upon heating the films at temperatures as low as 120 °C, a dramatic decrease in the resistance, of more than 6 orders of magnitude, was observed and led to the formation of strongly adherent conductive films. In a recent report, Prevo et al.[36] have described the flash annealing of Au nanoparticles on glass and polystyrene substrates. A convective assembly process, without any linker molecules, was used to deposit multilayers of Au on the substrate in one step. The have observed that flame or microwave treatment of the films caused coalescence of the particles and a change in the resistance of the films.

Characterization of the films by field-emission scanning electron microscopy (FE-SEM) and X-ray photoelectron spectroscopy (XPS) revealed an oxidation and desorption of the linker molecules. This causes the coalescence of the Au particles, which form more interconnected pathways without the insulating linker molecules, leading to decreased resistivities. The heating was done at three different temperatures: 120, 160, and 180 °C for different lengths of time. This led to a variety of different resistance values of the films. This approach provides an easy method for fabricating Au films with different resistivities, and the low-temperature processing makes it suitable for use on polymeric substrates. Applications of these films are envisaged in the fabrication of flexible electronic devices such as electrodes or resistors, and the low cost and easy processing makes it attractive for manufacturing.

Experimental Section

Materials. Kapton (2 mil thickness) was obtained from Dupont. Gold chloride trihydrate ($HAuCl_4 \cdot 3H_2O$), chlorotrimethylsilane, sodium citrate dihydrate, 2-mercaptoethanol (ME), and 1,6-hexanedithiol (HD) were purchased from Aldrich; 1,10-decanedithiol (DD) was purchased from Lancaster Synthesis (Pelham, NH), and 3-aminopropyltrimethoxysilane (APS) was purchased from Gelest. All the chemicals were used without further purification. All the water used was from an 18-MΩ Barnstead Nanopure water system

Fabrication of Au Film. The polymer surface was treated in argon plasma, and APS was deposited onto the surface. Details of the surface modification, APS deposition, and the synthesis of the Au colloid have been described previously.[35] The size of the Au colloids was 18 nm as measured by TEM. For the fabrication of the multilayer films, the APS-coated substrate was alternately immersed in the Au solution for 1 h and the linker molecule solution (4 mM ME in water, 4 mM HD in ethanol, or 4 mM DD in ethanol) for 15 min. The structures of the three linkers used are given in Figure 1. After each immersion the substrate was rinsed thoroughly with Nanopure water. For the UV−vis spectra, the films were fabricated on glass according to previously described methods.[21b] The spectra were recorded for glass substrates because Kapton has

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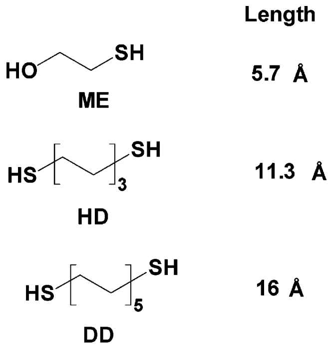


Figure 1. Structure and length of the linker molecules used.

a high absorbance in the UV−vis range. All the samples were heated in an air oven for the heating experiments.

Characterization. The resistance measurements on the film were made using both the two-point method and a four-point probe. The two-point measurements were made using a Sperry DM-350A digital multimeter. The measurements were obtained by touching the leads to two points of known separation distance on the film. The resistivity of the films was measured using a Mitsubishi Loresta MP MCP-T350 four-point probe and was also computed using the film geometry and resistance. Current−voltage (*I*−*V*) curves were obtained by a Keithley 236 source-measure unit; contacts were made by two leads attached to the films, by touching, about 1 cm apart.

Care was taken to ensure repeatability of the resistance measurements and reduce errors. When using the digital multimeter, the resistance of the probes themselves was calibrated and nulled to zero. This ensures that the resistance of the probes was not included when measuring the film resistance. Contact was made simply by touching the probes on the film surface. Contacts were made at marked points on the film, and the resistance did not change after repeated measurements on the same points, even for measurements repeated after a few days. The probes were gently touched on the film surface, and a slight pressure was applied until a value for the resistance was obtained. Applying more pressure did not change the resistance values; although too much pressure can tear the film giving inaccurate readings. When using the four-point probe, the instrument was calibrated against a control sample prior to taking measurements on the films. The contacts were again made at marked points on the sample, and the measurements were reproducible even after repeated measurements. The pressure applied in this case was more controlled as the probe was pressed onto the sample as much as the springs on the leads would allow, during all the measurements. For all the samples an average of at least three readings is reported.

The heating of the films was characterized by XPS using a Perkin-Elmer 5400 X-ray photoelectron spectrometer. The spectra were acquired using a Mg anode at an operating voltage of 14 kV. All the spectra were corrected with respect to the Au 4f peak at 84.0 eV. The surface of the films was observed by a Leo 1550 SEM operating at 5-kV accelerating voltage and an in-lens detector and a Nanoscope IIIa atomic force microscope. UV−vis spectra were obtained using a Hitachi U-2001 spectrophotometer.

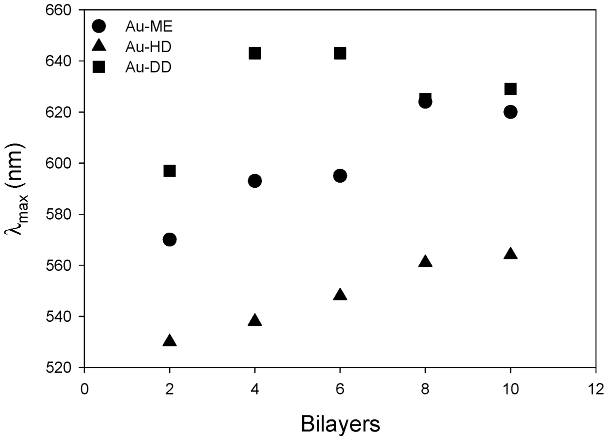


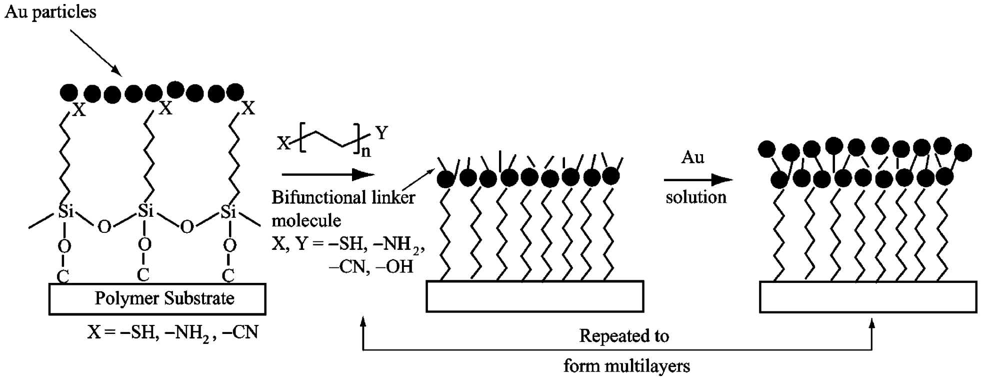
Figure 2. Absorbance peaks for Au−ME, Au−HD, and Au−DD films as a function of the number of bilayers deposited.

Results and Discussion

Fabrication of Au Multilayer Films. The films were fabricated by the LBL approach, and a general assembly strategy is shown in Scheme 1. The attachment of Au on polymeric substrates requires the deposition of a functional molecule that can bind to Au. This was achieved by the deposition of an amine-terminated silane after the substrate was plasma treated. The film is fabricated by the alternate immersion of the substrate in solutions of colloidal Au and linker molecules. The bifunctional molecule can bind to Au attached to the surface and can also lead to additional particle deposition. Repeated immersions in the two solutions leads to the fabrication of a shiny Au film, which has the visual appearance of bulk gold. Conductive films were deposited using this process on different polymeric substrates such as Kapton (polyimide) and polyethylene.

The growth of the films using the three linker molecules was studied by UV−vis spectroscopy. The spectra were recorded after drying the films fabricated on glass. Figure 2 depicts the absorption peak (λ_{max}) as a function of the number of bilayers deposited for the three different molecules (a bilayer refers to the layers formed after an immersion in Au followed by an immersion in linker molecule solution). It is

Scheme 1. Schematic Illustrating the LBL Assembly of Au/Linker Molecule Multilayer Films



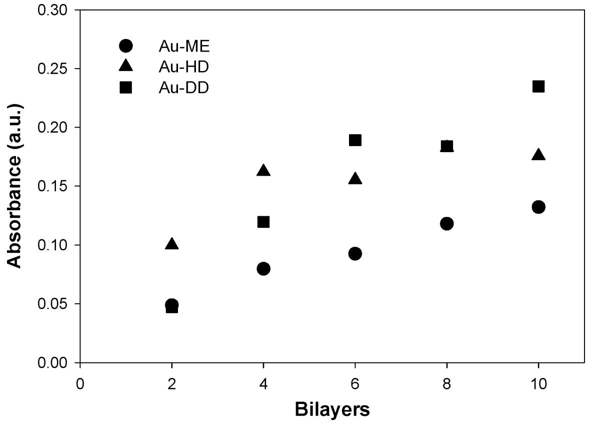


Figure 3. Absorption at 600 nm plotted as a function of the number of bilayers deposited for Au−ME, Au−HD, and Au−DD films. [Adsorption ploted for Au−DD is absorption measured/5, to fit within the scale of the plot.]

observed that there is a continual red shift in $\lambda_{\max}$ with the increase in the number of layers for ME and HD. For DD, there is a red shift up to about six bilayers after which there is a slight blue shift. This red shift is an indicator of the aggregation of the particles. As the number of layers increases, the particles attached to the surface start aggregating. This is confirmed by the broadening of the spectra upon addition of more layers (see Supporting Information). An increase in the absorbance with the addition of layers was observed, indicating successful attachment of Au (Figure 3).

A previous study[36] has reported the formation of Au multilayers without the use of linker molecules using a convective assembly process. The UV−vis spectra of these films also showed broad absorption peaks between 700 and 850 nm. This is an indication of a high degree of aggregation in the films. In contrast, the linker molecule films had much narrower peaks with the absorption maximum between 530 and 650 nm. Au colloidal dispersions are usually stabilized by coating them with organic molecules that prevent them from aggregating. The UV−vis results suggest a similar mechanism in the solid films also. The linker molecules prevent complete aggregation of the Au particles as was observed in the case of the films fabricated without it. The thickness of the films deposited by convective assembly was also much higher, about 400 nm compared to ∼85−130 nm for the linker molecule films.

The growth of the Au film on Kapton was monitored by measuring the direct current (dc) resistance. Figure 4 depicts the change in resistance of Au−ME and Au−HD films with increasing number of bilayers. Since the Au−DD films are not conductive even after deposition of 15 bilayers, the resistance as a function of the number of layers for Au−DD films could not be measured. From the figure it is observed that just after deposition of four bilayers the films start conducting. For the Au−ME films, there was some conductivity observed after three bilayers. However it was not uniform over the entire surface, and only some regions were conducting. After the deposition of another layer, the entire film becomes conductive, with the resistance being a few hundred ohms. The addition of more layers decreases the resistance to about a few ohms. For the Au−HD films, the starting resistances are more than 6 orders of magnitude higher, about a few MΩ. These films also become conducting after four bilayers, and addition of more layers decreases the resistance further, although the lowest resistance obtained was only about 1 MΩ. The length of the linker molecule has an important effect on the resistance of the films, as has been observed previously.[21b,22b] As the length of the linker increases, the resistance of the films also increases and our observations are in accordance with previous results. The dc resistance for the Au film deposited by convective assembly[36] was observed to be a function of the deposition speed. Higher speeds produced films where the percolation threshold for conduction was not reached and the particles were more separated. Similarly, in the films made using linker molecule films, longer molecules caused an increase in resistance due to the increased interparticle distance.

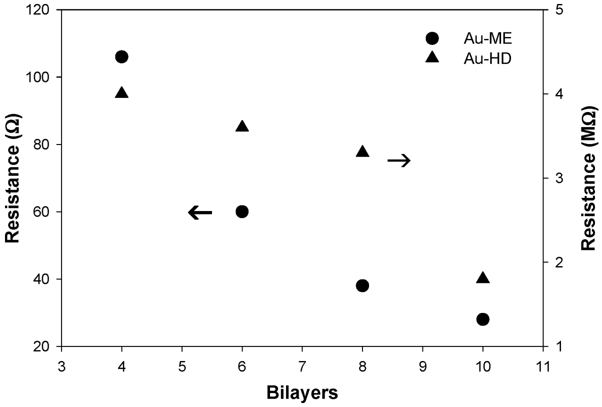


Figure 4. DC resistance of Au−ME and Au−HD films as a function of the number of bilayers deposited.

For the Au−ME films (11-nm Au particles), Musick et al.[21b] have observed that the resistance of the films on glass starts out very high, >10 MΩ, and that there is an exponential decrease in the resistance with increasing layers. The lowest resistances, of about a few tens of ohms, are achieved only after 10 bilayers. This is in contrast to our observations. They have also calculated a volume fraction of Au (V_{Au}) to be about 0.23 for 11-nm Au particles, and it remains constant for all coverages. Although the V_{Au} for the films on Kapton was not strictly calculated, an estimate can be made by using XPS data. XPS spectra were obtained for a four-bilayer Au−ME and Au−HD film at takeoff angles of 90°. The atomic concentrations of Au on the surfaces were obtained by calculating the area under the 4f peaks at 84.0 and 87.6 eV after correcting for sensitivity factors. The Au concentrations on Au−ME and Au−HD films were calculated to be 36.0 and 30.6%, respectively, which is the concentration of Au in the volume probed.[37] Hence, the V_{Au} can be estimated to be 0.36 for Au−ME and 0.31 for Au−HD. It should be noted that the electron escape depths are different for different elements and that influences the calculation of atomic concentrations; hence these values can at best be an upper estimate. This V_{Au} is in the range of volume fraction predicted for a 3-D array of conductors (0.3 for 3-D and 0.5 for 2-D).[38] For less than four bilayers, the surface coverage of Au is less. When the surface is examined

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(37) The area of the analyzed spot was 1 × 3 mm^2, and at 90° takeoff angles the depth probed is about 5 nm. Hence the volume probed is 1 mm × 3 mm × 5 nm.

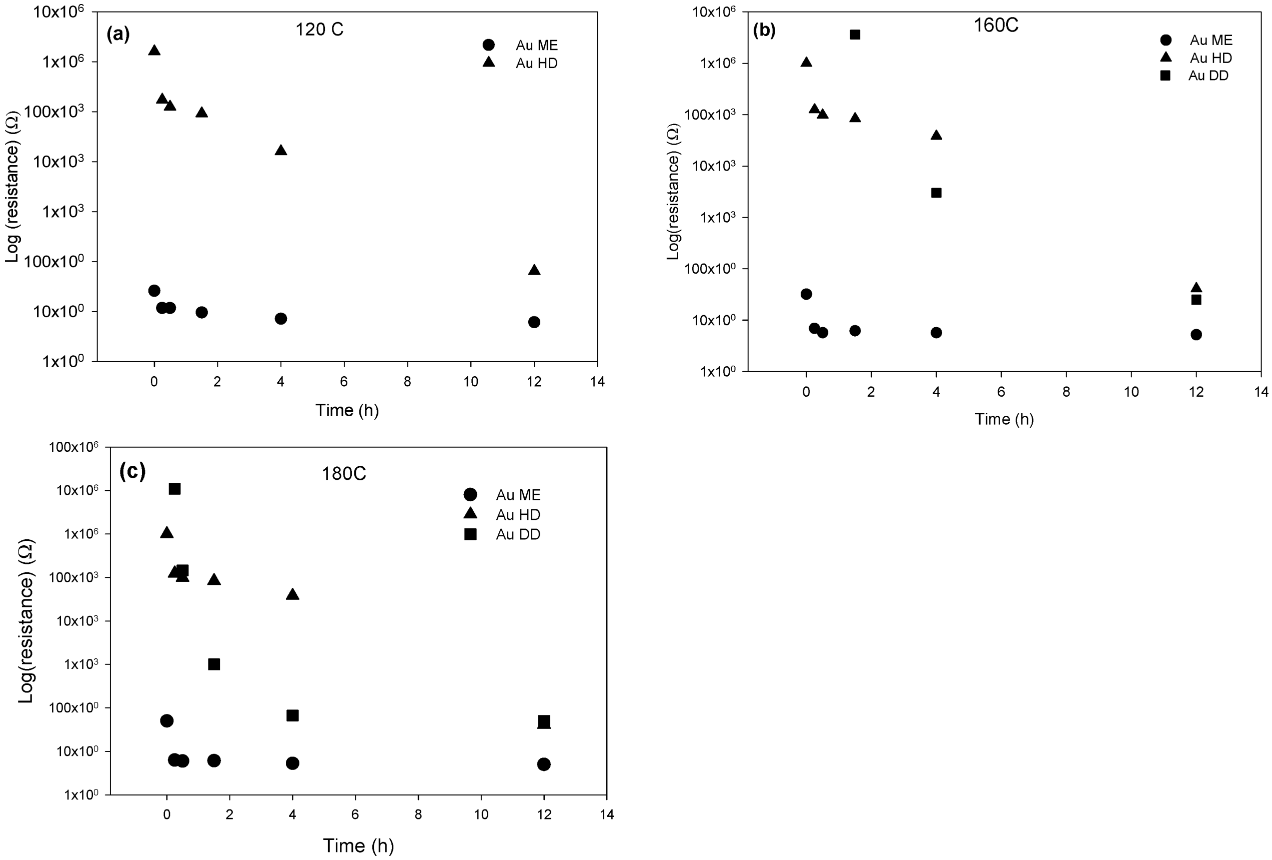

Figure 5. DC resistance of Au−ME, Au−HD, and Au−DD films as a function of time, heated at (a) 120 °C, (b) 160 °C, and (c) 180 °C.

with XPS, the Kapton surface is also visible, and the SEM images suggest that the coverage is mostly 2-D, and very few 3-D clusters are observed as compared to a four-bilayer film. This makes the film insulating in the case of Au−HD or conductive in a few places on Au−ME. For a Au−DD film, the Au atomic concentration was calculated to be only 23% from XPS even after 15 bilayers. Xu and Tao[39] have measured the resistance of single dithiol molecules and found that the resistance of the decanedithiol molecule (630 ± 50 MΩ) is much greater than that for a hexanedithiol molecule (10.5 ± 0.5 MΩ). This high resistance of the decanedithiol molecule coupled with the low Au atomic concentration makes the film insulating.

The V_{Au} for the 10-bilayer Au−ME and Au−HD films and the 15-bilayer Au−DD film was estimated to be 0.55, 0.43, and 0.23, respectively, using a similar approach. The V_{Au} for the Au−ME and Au−HD films are above the percolation threshold required for conductivity, while for the Au−DD films, it is not. This manifests in the decreasing conductivity for the Au−ME, Au−HD, and Au−DD films, in that order. However, using this method it is difficult to estimate the volume fraction for the linker molecules. Possible carbon contamination on the surface coupled with the low amounts of the linker molecules lead to high degree of error in the estimations.

Table 1. Resistivity (in. Ω·cm) of Au−ME, Au−HD, and Au−DD Films Heated at 120 and 180 °C for Different Times[a]

	10-bilayer Au−ME		10-bilayer Au−HD		15-bilayer Au−DD	
time	120 °C	180 °C	120 °C	180 °C	120 °C	180 °C
0	2.3×10^{-4}	2.3×10^{-4}	3.9	3.9		
1 h	1.4×10^{-4}	1.2×10^{-4}	0.5	0.2		2.9
12 h	1.5×10^{-4}	7.5×10^{-5}	1.7×10^{-4}	6×10^{-5}		2.4×10^{-4}

[a] The blanks in the table indicate films that are not conducting.

Heating of Au Multilayer Films. A decrease in the resistance of the Au multilayer films fabricated using the different linker molecules was observed upon heating. The films were heated at three different temperatures, 120, 160, and 180 °C, for different lengths of time in an air oven. The change in the resistance for Au−ME, Au−HD, and Au−DD films with time and temperature of heating is depicted in Figure 5. For the 10-bilayer Au−ME film, the resistance change is not much, as the resistance is low to begin with. However, there is a decrease observed with time and temperature. The resistance changes for the 10-bilayer Au−HD and 15-bilayer Au−DD films are more dramatic. For the Au−HD film, the resistance drops from ca. 1 MΩ to about 50 Ω after heating. This decrease occurs at temperatures as low as 120 °C; however, the time required for the decrease becomes greater at lower temperatures. The heating causes the nonconductive Au−DD film to become conductive; although the resistance changes are only observed at 160 and 180 °C. The resistivities of the films (Table 1) were measured using a four-point probe or were computed using the dimensions of the film (1 cm × 0.5 cm).[40] The thicknesses of the films was measured by cross-sectional SEM and were 86, 108, and 123 nm for 10-bilayer Au−

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(40) By use of the value of resistance R and the area A of the film = 0.5 cm (width) × 108 nm (thickness) (e.g., for Au−HD) and length L = 1 cm, the resistivity (ρ) was computed using the formula, $\rho = RA/L$.

ME, Au−HD, and 15-bilayer Au−DD, respectively. The lowest resistivities obtained, ca. 6×10^{-5} Ω·cm, were about 25 times that of bulk gold (2.4×10^{-6} Ω·cm).

The amount of Au particles on the surface is also important in changing the resistance by heating. Although four-bilayer films of Au−ME and Au−HD are conductive, upon heating these films, the Au−HD films were not conductive at all and the resistance of the Au−ME films is about a few hundred ohms. This suggests that, due to the coalescence caused by heating, there are more void spaces in the film and not enough connected pathways, as there is less Au, leading to lower or no conductivity at all. Hence, 10 bilayers were used as the optimum for the experiments on Au−ME and Au−HD. For the Au−DD films, heating 10 bilayers was not enough to make the film conductive and a minimum of 15 bilayers was required. Control experiments were performed by heating films fabricated on glass and Kapton by the seeding approach.[35] There was no change in conductivity even after heating the films at 200 °C, and no coalescence of the Au particles was observed upon imaging the films using tapping-mode atomic force microscopy (AFM, Supporting Information). To understand this resistance change upon heating, a number of different techniques were employed.

XPS. In a previous communication, the effects of heating a 10-bilayer Au−HD film were reported.[41] From the XPS data, it was observed that there was an oxidation and desorption of the linker molecules upon heating. This leads to the coalescence of the Au particles, creating more conductive pathways without the insulating linker molecule. The desorption of the molecules is better at higher temperatures. Similar results were obtained upon heating a 10-bilayer Au−ME film. The S 2p spectra of the unheated film showed a broad peak at 162.3 eV and a peak of lesser intensity at higher energy (169.2 eV). The lower-energy peak is attributed to S bound to Au as thiolate.[42,43] The higher energy peak is attributed to oxidized thiol. Previous studies have shown that thiols adsorbed on Au surfaces can undergo oxidation when exposed to ambient conditions.[44] Upon heating the films, the lower-energy peak decreased in intensity relative to the higher-energy peak. After being heated at 180 °C for 12 h, the S 2p peak almost disappeared, indicating the desorption of the linker. For the 15-bilayer Au−DD film, the S 2p peak for the unheated sample had a broad peak centered at ca. 163.8 eV, attributed to the Au−S thiolate linkage, and did not show any higher energy peak. Upon heating the films, an O 1s peak was observed, as well as a higher energy peak for S 2p centered at ca. 168.4 eV.

The S/Au ratios for the films heated at 120 and 180 °C for different lengths of time are given in Table 2. It is observed that as the time and temperature of heating increases, the ratio decreases, indicating the desorption of the linker molecules. As the length of the linker molecule increased, the S/Au ratios after heating also increased, indicating that lesser amounts of linker are desorbed at the same temperature as the length increases. Kodama et al.[45] have investigated the desorption of thiols from Au surfaces and have observed that, as the length of the alkyl chain increases, the desorption temperature increases. Other studies have reported desorption temperatures ranging from 100 to >200 °C for different thiols on Au surfaces.[46−48] In a report by Lala et al.,[49] thermogravimetric analysis of octadecanedithiol-capped Au particles revealed a 40% weight loss at 230 °C which was attributed to the desorption of the octadecanedithiol molecules. Another weight loss at 310 °C was attributed to the sintering of Au particles due to desorption of the stabilizing molecules.

Table 2. S/Au Ratios for Au−ME, Au−HD, and Au−DD Films Heated for Different Times and Temperatures as Calculated from XPS Data (Takeoff Angle = 90°)

	Au−ME		Au−HD		Au−DD	
time	120 °C	180 °C	120 °C	180 °C	120 °C	180 °C
0	0.09	0.09	0.22	0.18	0.37	0.37
4 h	0.08	0.04	0.17	0.09	0.45	0.16
12 h	0.11	0.06	0.14	0.08	0.2	0.13

The C 1s spectra for all the three heated films depicted a lower-energy peak at ca. 283 eV, apart from the hydrocarbon peak at 284.7 eV. This lower energy anomalous peak results due to differential charging in the heated samples. When a neutralizer was used while acquiring the spectra, the C 1s and O 1s peaks narrowed or broadened depending upon the neutralizer energy, and the anomalous C 1s peak could be completely eliminated. This suggests that there are regions of conductivity and regions where the film is not conducting. Heating the films causes an oxidation and desorption of the linker molecules. This causes the Au particles to coalesce and they form conductive regions, whereas the insulating linker molecules are either completely desorbed from the surface or clustered together forming the nonconducting regions leading to differential charging in the sample.

To eliminate the differential charging effect, the 15-bilayer Au−DD sample heated at 180 °C for 1 h was mounted onto the sample holder using conductive silver paint. The XPS spectra were acquired in this case with the neutralizer off. When the takeoff angle was 90°, three different Au 4f peaks (91.1, 87.7, and 84.0 eV) and two different peaks for C 1s (288.4 and 285.0 eV) were observed, compared to the two Au peaks (87.7 and 84.0 eV) and a single C peak (285.0 eV) for the samples that did not charge. When the takeoff angle was reduced to 15°, only two peaks for Au and a single peak for C was observed. The three peaks observed for Au at takeoff angles of 90° suggest that there are two different layers of Au separated by a layer of linker molecules. At 15° takeoff angles, when the depth analyzed is smaller, there are only two peaks observed, suggesting that only the topmost Au layer is visible. This hypothesis is supported by the observation of two C peaks at greater analyzed depths

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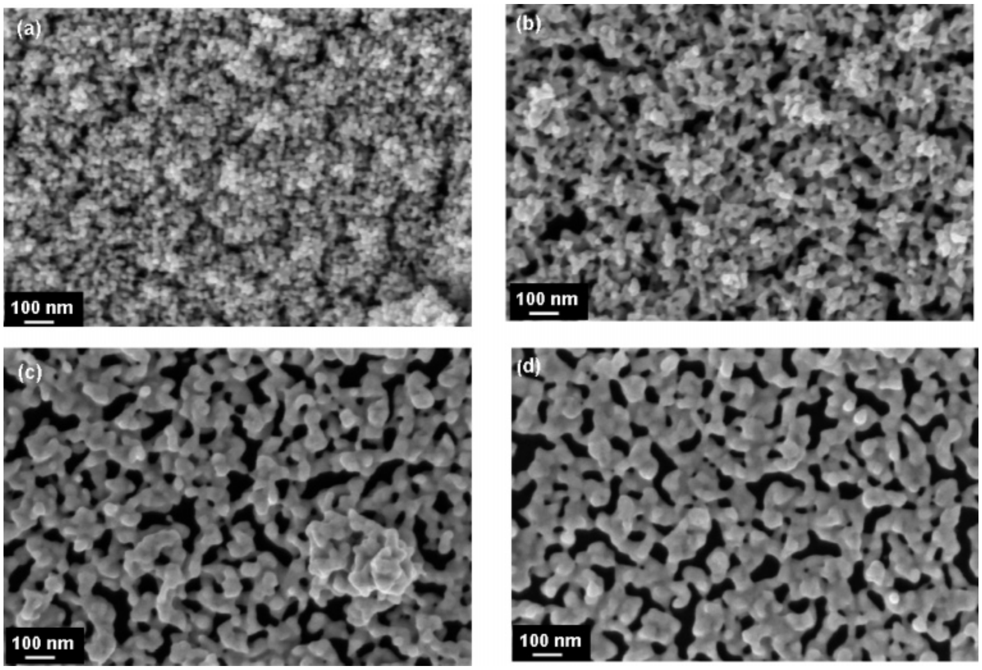

Figure 6. SEM images of a 10-bilayer Au−ME film (a) unheated and heated for 12 h at (b) 120 °C, (c) 160 °C, and (d) 180 °C.

and only one at lesser depths. Hence, it is reasonable to conclude that, upon heating the films, the Au particles coalesce together and the linker molecules are separated from the Au particles and form separate clusters. These then form separated layers of Au and linker molecules. From the XPS analysis of the films, it was observed that the S/Au ratio decreased upon heating. However, the linker molecules are not completely desorbed from the surface. So it is possible that the Au particles migrate to the surface upon heating.

SEM/AFM. Figure 6 depicts the SEM images of a 10-bilayer Au−ME film, unheated and heated at different temperatures for 12 h. The unheated film has a porous 3-D structure and individual spherical Au particles that are clustered together are clearly visible. Upon heating at 120 °C, the individuality of the particles is not clearly defined anymore and the particles start coalescing. This loss of individuality is clearer when the films are heated at 160 or 180 °C. The particles have completely coalesced, and the sphericity is lost. The coalescence is improved with increasing temperatures and causes better conductivity at higher temperatures. Similar results were obtained for a 10-bilayer Au−HD film. These results are similar to those obtained by Prevo et al.[36] They have annealed Au nanoparticles, deposited on glass or polystyrene substrates by a convective assembly, using flame or microwave treatment. However, in contrast to their observation that prolonged heating times changed the microstructure and caused the resistance to increase sharply, heating the Au/linker molecule films for >24 h did not change the microstructure further, nor was there any change in the resistance.

For the 15-bilayer Au−DD films, the SEM images were different. The formation of the film is not complete in all the regions. As seen in Figure 7a, there are regions of 3-D clusters, indicating regions where the film formation is complete and there are other regions where there is not much attachment of the Au particles. The reason for this is not clear. However, since all the other conditions for the deposition of the films are the same as for the Au−ME and Au−HD films except for the linker molecule, it seems that this effect is due to the linker molecule. This low coverage makes the film insulating. Upon heating the films at 120 °C, not much change is observed in the surface even after heating for more than 12 h (Figure 7b). No coalescence is observed, and the individual spherical Au particles are clearly visible in both the regions of 3-D clusters and regions of incomplete coverage. This is in accordance with the resistance values, which do not change upon heating at 120 °C, and the film is still nonconducting. However, upon heating at 180 °C, there is a coalescence observed, similar to the Au−ME and Au−HD films and the resistivity also decreases (Figure 7c). These observations suggest that, for the longer linker molecule, there is less adsorption of Au on the surface and that higher temperatures are required for the desorption of the molecule as observed in a previous study.[45]

The films were also characterized by AFM. Figure 8 shows a tapping-mode AFM height image of an unheated 10-bilayer Au−HD film and a film heated at 180 °C for 15 min. Before heating, the particles are smaller and spherical. After the film is heated, the coalescence of the particles is clearly visible. The particles no longer retain their original shapes and coalesce to form bigger particles of irregular shape. All the films have a high average roughness, between 20 and 40 nm, which does not change significantly after heating.

UV−vis Spectroscopy. UV−vis was another technique that was employed to characterize the coalescence process. All the UV−vis spectra were acquired on films deposited on glass. The spectra acquired for a 10-bilayer Au−ME film heated at 120 and 180 °C are depicted in Figure 9. For the film heated at 120 °C, a gradual broadening in the spectra is observed with increasing time of heating and the color of the sample becomes more purple than a dark pink. Upon heating at 180 °C, the opposite effect is observed. The spectra gradually become narrower and the color becomes pink rather than purple. A similar observation was made by Prevo et

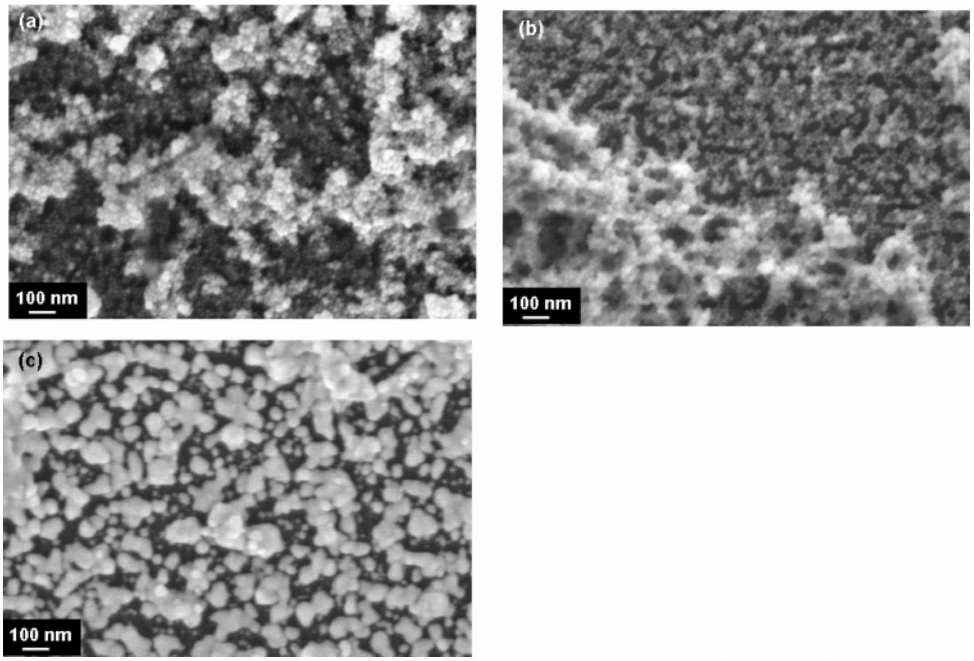

Figure 7. SEM images of 15-bilayer Au−DD films (a) unheated and heated for 12 h at (b) 120 °C and (c) 180 °C.

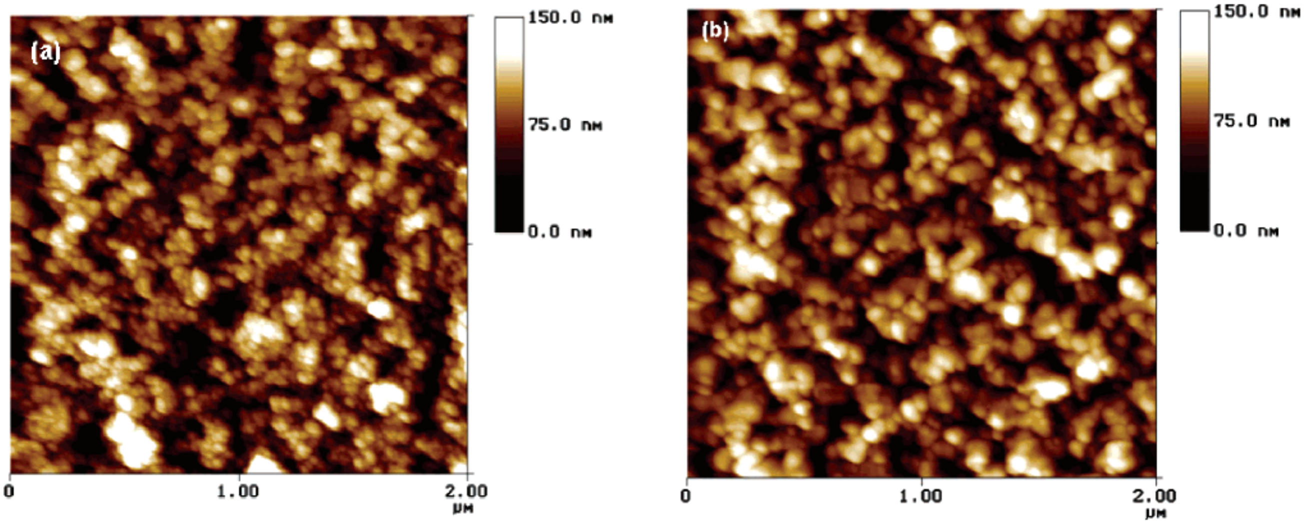

Figure 8. Tapping-mode AFM height images of a 10-bilayer Au−HD film (a) unheated and (b) heated for 15 min at 180 °C.

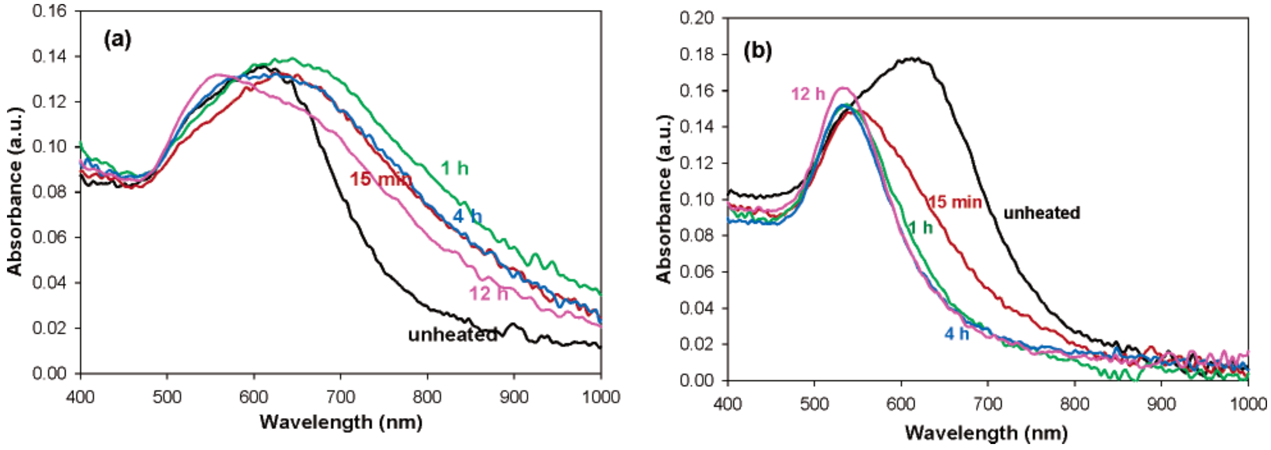

Figure 9. UV−vis spectra for a 10-bilayer Au−ME film heated for different lengths of time at (a) 120 °C and (b) 180 °C.

al.[36] on Au nanoparticle films flash annealed by a flame or microwave treatment. The $\lambda_{\max}$ and full-width at half-maximum (fwhm) for the 10-bilayer Au−ME and Au−HD films are given in Table 3, where fwhm is twice the difference between $\lambda_{\max}$ and the λ at which absorption is half the maximum.

Table 3. Absorption Peak and fwhm Values for 10-Bilayer Au−ME and Au−HD Films Heated at 120 and 180 °C for Different Lengths of Time

	10-bilayer Au−ME				10-bilayer Au−HD			
	120 °C		180 °C		120 °C		180 °C	
time	λ_{max} (nm)	fwhm (nm)	λ_{max} (nm)	fwhm (nm)	λ_{max} (nm)	fwhm (nm)	λ_{max} (nm)	fwhm (nm)
0	612	206	620	176	559	196	557	178
15 min	624	502	551	220	598	180	542	338
1 h	645	414	537	156	598	226	529	254
4 h	626	398	532	146	612	248	533	148
12 h	558	458	533	136	613	286	530	130

The absorption peak in the UV−vis spectrum for a colloidal Au film occurs due to excitations of the surface plasmons. The width of the peak provides information about the polydispersity of the particle sizes and the degree of aggregation. When the film is heated at 120 °C, the peak first broadens and then narrows slightly. However, the peak for the heated film is still broader than the unheated film. The broadening of the spectra is associated with aggregation and increase in particle polydispersity.[50] As the film is heated, the particles start aggregating. With increase in the time of heating, the aggregated particles start coalescing, breaking up the aggregation. This causes a slight narrowing of the peak. For the films heated at 180 °C, the peak width decreases with heating. This indicates that the coalescence has already begun within 15 min. The continued coalescence breaks up the aggregation, and for samples heated for 12 h, the peak is much narrower. Grabar et al.[12] have reported that the aggregation of Au colloids on surfaces causes a broad plasmon peak at 650−750 nm due to the coupling of the interparticle surface plasmons. With an increase in the interparticle spacing or decrease in aggregation, this peak disappears. From the SEM images of the heated film (Figure 6), it is observed that the heated films are less aggregated and more coalesced and hence have more interparticle spacing. This causes a narrowing of the peak width. Similar results were observed for the 10-bilayer Au−HD film,[41] except that the broadening of the spectra for the films heated at 120 °C was lesser than for the Au−ME films.

For the 15-bilayer Au−DD films, no change in the UV−vis spectra was observed upon heating at 120 °C. This is because there is no coalescence occurring as evidenced by the SEM images and no change in the resistance. Upon heating at 180 °C, there is a continual broadening of the peaks. After heating for 12 h, a very broad peak extending from 550 to 1000 nm is observed. From the SEM image (Figure 7) it is observed that although there is coalescence of particles, there are many single particles or small clusters observed. This leads to the broadened spectra due to high polydispersity of particle sizes. From the above observations it is believed that the coalescence process occurs first by aggregation of the particles, following desorption of the linker and subsequently the aggregated particles coalesce. These observations suggest that apart from the electrical properties, the optical properties of the films can also be tuned using this approach.

***I*−*V* Measurements.** Current−voltage (*I*−*V*) measurements were performed on the films to understand the nature of the conductivity of the samples. All the films showed linear *I*−*V* curves in the voltage range measured (−10 V to 10 V), indicating that the resistance is ohmic. There was no hysteresis observed in any of the films when repeated measurements were made. The resistance did not change due to heating caused by the passing of current even after repeated cycles of measurement. The resistance of the films was measured from the slope of the curves, and the values measured were in agreement with the resistances obtained using the digital multimeter. A representative set of curves are depicted in Figure 10. The resistance of the films is given by the reciprocal of the slope of the curves ($R = V/I$). Hence, the higher the slope, the lower is the resistance. From Figure 10a, it is observed that the film heated for 12 h has the highest slope and hence has the lowest resistance. A magnification of the curves for the unheated film and the film heated for 1 h is shown in Figure 10b. The slope for the film heated for 1 h is higher than the slope of the unheated film, indicating that the resistance for the unheated film is higher.

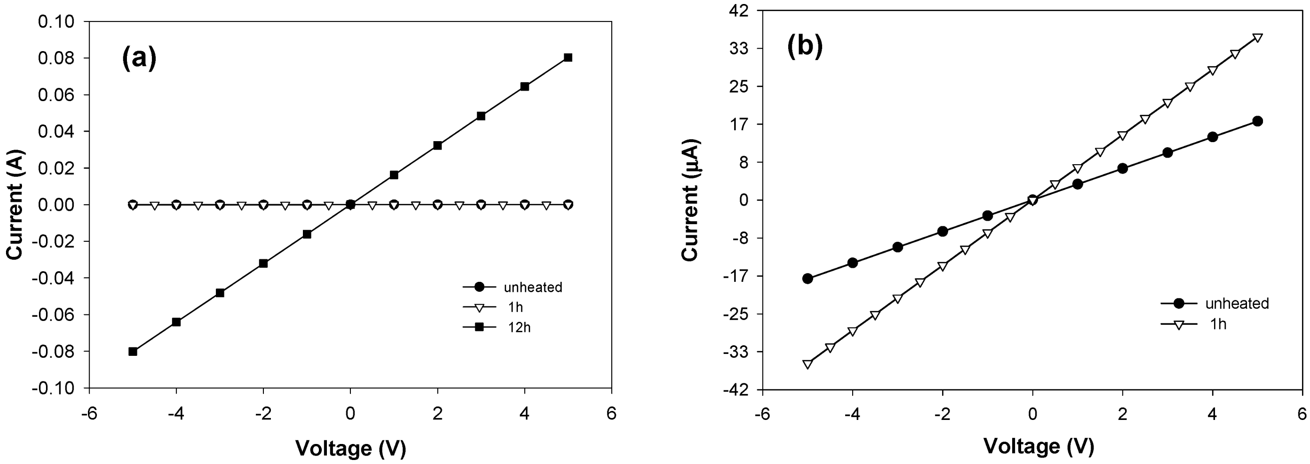

Figure 10. Current−voltage curves for a 10-bilayer Au−HD film (a) unheated and heated at 120 °C for 1 and 12 h; (b) magnification of the unheated and 1 h curves from a.

Adhesion Tests. A qualitative analysis of the adhesion of the Au film to the Kapton substrate was made using the tape-peel test. An adhesive tape was pressed firmly onto the film and was slowly peeled off. The amount of material transferred onto the tape gives an estimate of the adhesion of Au to the substrate. For the unheated and heated films, rinsing the films in water or ethanol, twisting or bending the film, or rubbing the film manually did not remove any gold. However, upon using the tape peel test on the unheated films, a significant portion of the film was transferred to the tape, indicating that the adhesion is not very good. The adhesion improves greatly upon heating the films. The films heated for the longest time or higher temperature had the best adhesion. No significant amount of gold was transferred onto the tape for any of the samples heated at 180 °C for any length of time. At lower temperatures, the adhesion improved with longer times of heating. These observations are in contrast to those made by Prevo et al.,[36] where it was observed that the adhesion of the flash annealed Au nanoparticle films to the substrate was poorer than the films that were not annealed.

The T_g of Kapton is greater than 300 °C, and the material is thermally stable for continuous use to about 200−220 °C (from manufacturer specifications). The temperatures used in this study are much lower than that. Heating a bare Kapton film at these temperatures produced no observable changes in the film. However, it is possible that, upon heating, the Au particles penetrate into the silane layer or even into the Kapton film, more than in the unheated samples, causing better Au adhesion in the heated films. Such a penetration of Au particles into the polymer matrix has been observed previously by Kunz et al.[51] on poly(vinyl pyridine) surfaces.

Conclusions

Colloidal Au multilayer films were fabricated on a flexible polymeric substrate (Kapton) using three linker molecules having different lengths. The resistance of the films was found to be a function of the linker molecule length, with longer molecules having higher resistance. Heating the films at temperatures as low as 120 °C caused a decrease in the resistance of the films. This decrease occurs due to the oxidation and desorption of the linker molecules, leading to the coalescence of the Au particles forming more conducting pathways. As the films are heated, the linker molecules desorb causing the aggregation of the Au particles. As the heating is prolonged, the Au particles that have aggregated start coalescing causing a decrease in the resistance. This hypothesis is supported by the SEM and UV−vis data. At lower temperatures the coalescence is not complete, and the particles are mostly aggregated. This aggregation can be broken either by increasing the temperature or by increasing time at lower temperatures. Apart from the length of the linker molecule, the resistance of the films was observed to be function of the time and temperature of heating, and a variety of different resistances can be obtained merely by changing any of these parameters. The resistance of the films was found to be ohmic and was not affected by the heating caused by current flow even after prolonged cycles of measurement, suggesting that these electrodes can be used in small electronic devices. In the temperature range studied, the Au−ME and Au−HD films behaved similarly, whereas the behavior of the Au−DD films was slightly different. Since this method does not require any sophisticated equipment or controlled fabrication conditions, it provides a convenient and cost-effective method of fabricating and controlling the electrical and optical properties of Au films. The low-temperature processing makes it suitable for use on flexible polymeric substrates also, apart from substrates such as glass or silicon, and can be employed in the fabrication of flexible optoelectronic devices.

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Supporting Information Available: UV−vis data for growth of Au−ME, Au−HD, and Au−DD and tapping-mode AFM height image of seeded and heated Au on Kapton. This material is available free of charge via the Internet at http://pubs.acs.org.

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