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Nanoscale induced formation of silicide around gold nanoparticles encapsulated in a-Si.

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Abstract

Decorating thin film solar cells with plasmonic nanoparticles is being pursued, in order to improve device efficiency through increased scattering and local field enhancement. Gold nanoparticles are in particular interesting, due to their chemical inertness and plasmon resonance in the visible range of the spectrum. In this work, gold nanoparticles fabricated by a gas aggregation nanoparticle source and embedded in a-Si (a commercial solar cell material) are studied using x-ray photo-electron spectroscopy, transmission electron microscopy, electron energy-loss spectroscopy and energy dispersive X-ray spectroscopy. The formation of gold silicide around the nanoparticles is investigated, as it has important consequences for the optical and electronic properties of the structures. Differently from previous studies, in which the silicide formation is observed for gold nanoparticles and thin films grown on top of crystalline silicon or silica, it is found that silicide formation is largely enhanced around the nanoparticles, owing to their increased surface/volume ratio. A detailed gold silicide formation mechanism is presented based on the results, and strategies for optimizing the design of plasmonically enhanced solar cells with gold nanoparticles encapsulated in a-Si are discussed.
Introduction

Plasmonic nanoparticles have been shown to enhance the optical absorption of thin film solar cells and photodetectors. Through localized surface plasmon resonances (LSPRs), these nanoparticles increase both the scattering and the optical absorption of the incident light, resulting from the plasmonic near-field enhancement close to the metal nanoparticle surface. Specifically, the LSPRs of Au nanoparticles have improved the incident optical absorption in Si nano-membrane Schottky barrier diodes, n-CdSe/p-Si heterojunction diodes and a-Si thin films. Furthermore, the gold plasmonic interaction with silicon nanocrystals can enhance the luminescence emission rate. Although these studies highlight the potential of using Au nanoparticles to engineer high efficiency photodetector and photovoltaic solid state devices, the presence of intermediate states at the Au nanoparticle/Si interface need to be taken into account, unless the gold nanoparticles and silicon surface are well separated. Moreover, embedding plasmonic nanoparticles in semiconductor layers is often pursued as a viable solution to avoid degradation of the nanoparticles in solar cell devices. The Au/Si interface has been extensively studied in the past in order to understand both its potential as a metal/silicon contact and the fundamental thermodynamics of the growth process at the Au/Si interface, which is for example very important for growing novel silicon nanowires with gold catalysts. The presence of a silicide with composition near the eutectic point of the Au/Si phase diagram has been observed with Auger electron spectroscopy (AES), He+ ion scattering, synchrotron radiation photoemission spectroscopy (PES), time of flight secondary ion mass spectroscopy (TOF-SIMS) and x-ray photoelectron spectroscopy (XPS), even for AuSi clusters. Since gold is a nonreactive noble metal, the improbable formation of a silicide, even at room temperature, has motivated numerous theories regarding the formation and abruptness of the interface. However, all these studies involved the deposition of an Au evaporated film on top of either a c-Si or a-Si substrate. Other studies have examined gold nanoparticles deposited on top of SiO2 or Si surfaces followed often by thermal or by electrochemical treatments. Plasmonic nanoparticles, however, are known to have optimal light scattering efficiencies when embedded inside the semiconductor layer of a solar cell. With technological advances allowing synthesis of gold nanoparticles of controllable size and shapes and combining them with (a-Si) thin semiconductor films, the reverse deposition sequence, i.e. silicon on gold may lead to a different silicide growth process, which is for example also important for the catalytic growth of silicon
nanowires on gold particles\textsuperscript{18}, using gold particles as template for silicon nanopillar fabrication by reactive ion etching\textsuperscript{38} or for biomedical application where gold-silicon particles can be used for cancer treatment\textsuperscript{39} and immune sensing\textsuperscript{40}. Therefore, the formation of the Au/Si interface in embedded gold nanoparticles must be revisited to gain insight on the growth mechanism of such nanostructures.

In the present work, we report on the interface between gold nanoparticles synthesized by a gas phase aggregation cluster source and embedded by an overlaying magnetron sputtered a-Si thin film, both operated at room temperature. The results of the a-Si layer on top of the gold nanoparticles were compared to the interface of magnetron sputtered a-Si deposited on top of a gold evaporated film. The presence of intermediate gold and silicon states at the gold nanoparticle/Si interface is investigated by X-ray photoelectron spectroscopy (XPS) measurements. The results are supported by (scanning) transmission electron microscopy (S)TEM imaging, electron energy-loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy EDX. Based on the findings, a theoretical mechanism for the silicide formation at an Au/Si interface is presented and discussed. The valuable insight obtained has significant implications for the design of devices including plasmonic gold nanoparticles embedded within a-Si, such as solid state photodetectors and ultrathin film photovoltaic cells.

**Experimental**

Three types of samples have been investigated in this work: a-Si deposited above an approximately 80 nm thick Au film grown via thermal evaporation (a-Si/AuEvap), 25 nm (diameter) Au nanoparticles (AuNP25nm) and 25 nm Au nanoparticles embedded in a-Si (a-Si/AuNP25nm). The gold nanoparticles were deposited with a gas aggregation nanoparticle source based on magnetron sputtering (NC200U-B Oxford Applied Research Ltd.)\textsuperscript{41,42} on glass with ITO (80 nm) substrates. A schematic cross-sectional representation of the samples is given in Fig. 1. For the deposition of nanoparticles, argon gas was used as both sputter and carrier gas inside the gas aggregation chamber with a flow rate of 15 sccm. All deposition were performed at room temperature and no thermal treatments were performed. The Au target had a purity of 99.99%, the magnetron DC power was 30 Watts and the aggregation length was 60 mm for all samples. The conformally grown a-Si thin film on the a-Si/AuNP25nm and a-Si/AuEvap samples were fabricated by magnetron sputtering with a power of 124 W and the argon flow of 40 sccm from a polycrystalline silicon target (99.9%). The thickness of the deposited a-Si film was controlled through deposition time, which was 50s for the a-Si/AuNP25nm sample and 100s for the a-Si/AuEvap sample. The a-Si film in the a-Si/AuEvap sample was 6 nm thick with an accuracy of ± 2 nm, determined by a profilometer (KLA-Tencor stylus profiler). The a-Si/AuNP25nm film thickness was approximated using the
Figure 1. Schematic depiction of A) a-Si/AuEvap sample where a 6nm a-Si film is grown above a thermally evaporated 80 nm Au film. B) AuNP25nm sample where Au nanoparticles are deposited on ITO. C) a-Si/AuNP25nm sample where Au nanoparticles are embedded within an a-Si thin film. The near side of the schematic shows the nanoparticles lying below the surface while the far side of the schematic shows the raised a-Si surface resulting from the presence of gold nanoparticles below.
attenuation of the Au 4f doublet XPS signal (supplementary material), since deposition time of 50 s is expected to produce a thickness <3 nm. Determining the thin film thickness with the profilometer was challenging due to substrate roughness. Based on the attenuation calculation, the approximate thickness of the a-Si layer is indeed 3 nm.

Gold nanoparticles and a-Si layers were also deposited on silicon nitride TEM grids using an identical procedure to that described above. The TEM grids contain nine windows, which are 5 nm thick each (SiMPore, SN100-A05Q33A). The TEM, EELS and EDX measurements were performed with a FEI Titan TEM equipped with a monochromator and a probe aberration corrector. The microscope was operated in STEM mode with the acceleration voltage of 120 kV. The morphological characteristics of the sample-surfaces were determined by atomic force microscopy (AFM) using a Bruker-Catalyst Atomic Force Microscope in Peak-Force Tapping® mode in air, equipped with ScanAsyst-AIR tips.

The XPS measurements were acquired with a Leybold LHS 10/12 UHV apparatus equipped with a hemispherical electron analyzer and a conventional X-ray source (Al Kα = 1486.6 eV). The element-specific narrow-range spectra were acquired in constant step energy mode with E_{pass} = 30 eV. The overall energy resolution was 0.9 eV. The pressure in the experimental chamber during experiments was below 5 × 10⁻⁹ mbar. All spectra were scaled to the Fermi level and the binding energy scale was calibrated via the Au 4f_{7/2} core level line (located at 83.97 eV) of a clean polycrystalline Au sample.

Voigt line-shape was used to fit the Au 4f doublets of the a-Si/AuEvap, AuNP25nm and a-Si/AuNP25nm samples, fixing the area ratio for the two spin orbit peaks (4f_{5/2} : 4f_{7/2}) at 3:4. The Shirley background was included in the fit. A shoulder at higher binding energy is observable in the a-Si/AuNP25nm sample, thus a second doublet was added to the fit. Least square curve-fitting was performed using the programs KolXPD and Igor Pro (Wavemetrics). The evaluation of the quality of the fit was assessed by applying the Abbe criterion on the residuals. The fit was considered acceptable if the Abbe parameter results to be 1.0 ± 0.2.

To investigate the Au/Si interface as a function of a-Si thickness, the a-Si/AuNP25nm sample was sputtered at three minute intervals with a Leybold IQP 10/63 Penning discharge ion source operated with Argon gas. The sputtering rate was held constant by fixing the accelerating potential to 0.5 KeV.

**Results and discussion**

*3.1 AFM analysis of a-Si/AuNP25nm sample*

A representative AFM image of the a-Si/AuNP25nm sample is shown in Fig. 2. Randomly distributed individual objects are visible on the surface, which confirms that the sample consists of Au nanoparticles
with a height, taken as an effective measure of the nanoparticle size, of about 20 nm. The nanoparticles are indeed isolated from one another and remain unaltered in size during the a-Si deposition as the relative height remains the same. The lateral length is larger than the height due to the AFM tip convolution. This gold nanoparticle morphology, with an effective surface coverage of 40 nanoparticles µm\(^{-2}\), results in a unique nanostructure for the a-Si to interact with during deposition. In comparison to the continuous layer of evaporated gold in the a-Si/AuEvap sample, the gold atoms of the Au nanoparticles have a lower number of nearest neighbors and therefore a localized highest occupied molecular orbital.\(^{44}\)

**Figure 2.** AFM Image of a-Si/AuNP25nm sample. The effective surface coverage is 40 nanoparticles µm\(^{-2}\). (Top right) A typical AuNP25nm feature of approximately 25 nm in height.
TEM analysis of a-Si/AuNP25nm Sample

Cross-sectional view

High-angle annular dark field (HAADF) STEM images of an a-Si/AuNP25nm sample captured in cross-sectional geometry after focused ion beam milling of the sample are shown in Fig. 3. The intensity of the images is related primarily to the atomic number of the atomic species present in the sample. The images confirm that the Au nanoparticles are embedded in the a-Si matrix, as well as indicating regions in Fig. 3a with unexpected gold content. These regions, outlined in red in Fig. 3b, can suggest diffusion of gold into the a-Si matrix. The gold atoms appear to have diffused nearly to the surface of the a-Si thin film, producing an irregular interface that will complicate the electrical and optical properties of the material.
surrounding silicon. The far left Au nanoparticle in Fig. 3a appears to have not lost gold to the surrounding a-Si matrix. This suggests that the diffusion process may be affected by many factors such as local density, defect states and degree of crystallinity within the a-Si layer\textsuperscript{47}.

Figure 4. a) STEM image of gold particles embedded in a-Si b) EELS spectrum of Au N,\textsubscript{6,7} edge and Si L\textsubscript{2,3} edge. EELS maps of c) Au, d) Si and e) SiO part of the EELS spectrum. A gold and oxygen signal is clearly present outside the gold nanoparticle area.
Plan-view STEM – EELS analysis

A HAADF STEM image of the aSi/AuNP25nm sample in plan-view geometry is shown in Fig. 4a. The outdiffusion of Au from the left NP into the surrounding a-Si matrix is clearly visible in the image (marked by an arrow). Besides this, a different contrast is clearly present directly around all three NPs compared to the a-Si matrix elsewhere. To identify the origin of this contrast, Si L_{2,3} and Au N_{6,7} edges in the region enclosed within the marked rectangle in Fig. 4a were examined with EELS. A representative EEL spectrum is shown in Fig. 4b. The integrated intensity maps of the features corresponding to Au, Si and SiO2 are displayed in Fig. 4 c-e. The map in Fig. 4c confirms that the region of high intensity next to the NP on the left contains Au. In addition, the presence of a more uniformly distributed region containing smaller amounts of Au around all three NPs is observed. Surprisingly, the results also indicate a higher concentration of SiO\textsubscript{2} around the NPs. This increase is beyond what can be explained in terms of sample geometry and is corroborated with EDX, which shows a doubling of the O content around the particles compared to the rest of the a-Si matrix (SM Fig 3). This preferential oxidation could have been caused due to differences in porosity or concentration of defects in a-Si (induced by the presence of gold) in the regions around the NPs. It is important to point out that the EELS analysis was carried out several months after the fabrication of the sample and this time lapse has contributed to this enhanced oxidation of the sample. In contrast, the XPS analysis presented in the following section was performed within a month of sample fabrication and will offer further insight into the possible interaction that has occurred between the a-Si matrix and the Au nanoparticles.

XPS measurements of a-Si/AuEvap, AuNP25nm and a-Si/AuNP25nm Au 4f doublet

The XPS spectra of the Au 4f edge for a-Si/AuEvap, AuNP25nm and a-Si/AuNP25nm samples are shown in Fig. 5. Previous studies on the Au/Si interface mainly deal with the deposition of gold onto either crystalline or amorphous silicon substrates \textsuperscript{19–24,26–28}. In these structures, the formation of a gold silicide is indicated by the arising shoulder at higher binding energy in Au 4f lines, as widely observed for composition near the eutectic point of the Au/Si phase diagram \textsuperscript{23,24}. The Au 4f spectrum of the a-Si/AuEvap shows the narrow profile of pure gold with the Au 4f\textsubscript{7/2} peak located at 84.0 eV, without a shoulder feature evident of silicide formation. This suggests that a reverse sequence of growth, i.e. deposition of a-Si layer on top of a thermally evaporated gold film, does not lead to the formation of silicide. A possible explanation is that metallic bonding between neighboring Au atoms favors
**Figure 5.**

**a)** The change in the Au4f doublet in the a-Si/AuNP25nm sample with 3’ sputtering intervals. After 6’ the AuSi4f doublet begins to decrease in intensity. 

**b)** The ratio of the AuNP4f : AuSi4f doublet area. A linear increase in the AuNP4f area after 6’ of sputtering highlights the removal of the silicide from the sample. Error in the area ratio calculated at each sputtering step in minimal because the tolerance of the fits was set to $10^{-6}$. 

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**Normalized Intensity (a.u.)**

**Binding Energy /eV**
Figure 6. Au 4f XPS spectra. a) Evolution of the Au 4f doublet in the a-Si/AuNP25nm sample with 3’
sputtering intervals. b) Ratio of the Au_0 4f : Au-Si 4f doublet area. A linear increase in the Au_0 4f area
after 9’ of sputtering highlights the removal of the silicide from the sample.
the growth of a compact film, which hampers an effective migration/diffusion of atoms at RT. This also points to a minimal effect of the argon sputter plasma on the gold layer. A broadening of the Au 4f lines of the AuNP25nm and a-Si/AuNP25nm samples compared to that of the a-Si/AuEvap sample is seen in Fig. 5. It is well known that nanoparticles of decreasing size show a chemical shift towards higher binding energies, originating from size-dependent surface states. 48,49 The observed change in the FWHM is related to the nanoparticle size distribution and therefore most likely due to the change from a continuous gold film to a nanostructure of partially isolated gold nanoparticles of varying sizes. 50 Also the position of the Au 4f/2 peak for the AuNP25nm is located at 84.0 eV, with a spin-orbit splitting of 3.7 eV. The deconvolution (Fig. 5) of Au 4f/2 line of the a-Si/AuNP25nm shows the presence of two peaks at 84.3 eV and 85.5 eV, where the former is a metallic gold and the latter gold in silicide phase.

**Au 4f and Si 2p signal evolution of a-Si/AuNP25nm sample with sputtering time**

Because the Indium 3d XPS signals (SM Fig 1) from the substrate remained at the same binding energy of 445.1 ± 0.02 eV during all XPS measurements, it can be concluded that no charge accumulated on the a-Si/AuNP25nm sample after the sputtering steps. The XPS signals of the Au 4f doublets at each sputtering step are shown within Fig. 6a. The shoulder of the Au 4f doublet does not shift as a function of sputtering time, placed at 1.1 eV towards higher BE and the spin orbit splitting of 3.7 eV. The binding energy shift is consistent with previous reports on the Au/Si interface, in which it ranges from 0.6 to 1.2 eV26–28,51. Therefore it is conceivable that a silicide has been formed within the a-Si/AuNP25nm sample 23,26,52. At sputtering times above 0′ the ratio of the Au/0 4f doublet area to the Au-Si 4f doublet area increases linearly (Fig. 6b) due to the gradual removal of the silicide interface.

In Fig. 7 the change in the a-Si/AuNP25nm Si2p signal shows that as the silicide interface is removed, a simultaneous shift in the Si 2p peak to higher binding energy occurs. This portion of the Si 2p peak is interpreted as Si participating in silicide bonds. Previous studies have identified a higher binding energy Si 2p peak at approximately 0.65 eV and explain this shift as a result of charge transfer to the more electronegative gold atoms.20,22,23,26 This theory is confirmed by the difference in normalized signal intensity of the Si 2p peaks between sputtering steps as shown in Fig. 7b. A peak at 99.63 eV is initially removed from the Si 2p signal within the first 6′ of sputtering. The next 9′ of sputtering (from 6′ to 15′ in Fig. 7b) removes a broader peak at 99.87 eV. Since this shift in binding energy is only 0.24 eV it should not be confused with Si reacting with oxygen to form Si2O, which results in a peak at 0.95 eV above pure silicon 53. Fig. 7b shows that the intensity of the Si 2p peak diminishes with incrementing sputtering time,
while the intensity of the SiO$_2$ signal increases mainly after the removal of the silicide Si 2p peak. This means that most of the SiO$_2$ within the sample is located on top of the ITO substrate instead of on top of

![Figure 7](image)

**Figure 7.** a) Evolution of the Si 2p peak in the a-Si/AuNP25nm sample with 3’ sputtering intervals. The Si$_0$ peak shifts towards higher binding energy mirroring the evolution of the Au-Si 4f doublet. The intensity of the SiO$_2$ feature increases without any significant energy shift. b) The difference in the normalized Si 2p signal between the spectra acquired after 6 min of sputtering and without the sputtering (6’ – 0’) and between 15 min and 6 min of sputtering (15’ – 6’). Negative values in these plots refer to states being removed between the two sputtering times, positive values correspond to an increment of states. The plots highlight the loss of the lower energy component of the Si$_0$ peak showing a shift of 0.24 eV.
the a-Si thin film coating the Au nanoparticles. The presence of SiO$_2$ at the ITO/a-Si interface is the result of an interface reaction between ITO and Si because of silicon’s higher affinity for oxygen, which produces an ITO-SiO$_2$-Si interface similar to those observed in previous studies. $^{54,55}$ Interestingly, since the SiO$_2$ signal does not decline prior to the removal of silicon, it is possible that a reduced reactivity in the topmost layer of silicon is caused by the silicide formation.$^{35,56}$ The disappearance of the higher binding energy Si 2p peak after the disappearance of the pure Si signal, confirms that the silicide regions are located between the Au nanoparticles and the a-Si.

From the above analysis of the shifts in the Au 4f and Si 2p doublets, a schematic diagram of the charge flow between Au atoms and Si atoms that results in silicide formation is summarized (Fig. 8). An initial a-Si layer is formed with partially occupied sp$^3$ hybridized dangling bonds (Fig. 8a). Gold atoms then diffuse from the surface of Au nanoparticles into interstitial regions of the a-Si lattice as their hybridized s-d orbitals donate charge to the a-Si dangling bonds (Fig. 8b). The presence of the gold atoms further weakens the Si-Si backbone of the a-Si structure and leads to the donation of sp$^3$ electrons from Si to the more electronegative Au atom (Fig. 8c). $^{23,30,57,58}$ The silicide therefore carries no net charge, but the delocalization of Au 5d electrons from the Au atom leads to a shift in the Au 4f doublet to higher binding energy, counterintuitive to the electronegativity of the atom.$^{59}$ A fully developed gold rich silicide likely possesses the eutectic point composition with the Au and Si valence electrons shared equally between both atoms (Fig. 8d). This process is not expected to occur uniformly around the Au particles since cross-sectional and plan-view STEM images of the a-Si/AuNP25nm sample indicate an inhomogeneous diffusion of Au into the surrounding a-Si matrix.

The presence and movement of interstitial gold atoms responsible for silicide formation has been accurately described by the kick-out mechanism developed by Gösele et al.$^{60}$ This mechanism asserts that fast diffusing interstitial Au atoms displace Si atoms in the a-Si lattice and form immobile Au substitutes within the Si lattice. The displaced Si atoms form self-interstitials, which supersaturate the interface and discourage further gold diffusion. It is expected that this mechanism is also at play within the a-Si/AuNP25nm sample of this work and ultimately leads to an equilibrium point where there is no further net movement of Au atoms into the a-Si interstitial sites. However, the limited thickness of the a-Si thin film can hinder the process, explaining the higher concentration of gold in the a-Si thin film on top of the gold nanoparticle. Over all, it is expected that gold nanoparticles embedded within a-Si thin films should not be subject to a continuous silicide reaction as the sample ages. Therefore, a-Si layers grown under similar conditions should exhibit similar Au nanoparticle/a-Si interfaces with stable and predictable plasmonic response.
**Figure 8.**

**a)** The initially deposited a-Si layer possesses partially occupied sp\(^3\) orbitals highlighted in red. The Si-Si backbone is weakened and sp\(^3\) electrons feel the presence of the highly electronegative Au atom. **b)** Diffused Au atoms (yellow circles) donate s-d hybridized electrons (blue) to the sp\(^3\) orbitals of a-Si. Further weakening of the Si-Si backbone occurs and sp\(^3\) electrons (green arrows) are donated back to the Au atom. **c)** Molecular orbitals are formed as the silicide is stabilized. Valence electrons are now delocalized from Au and Si atoms leading to Au 4f and Si 2p core levels shifting to higher binding energy.
Because the formation of a silicide occurs only in the a-Si/AuNP25nm sample, this implies that the affinity of gold for the dangling bonds found within the a-Si layer is highly dependent on the nanostructure of the gold. When gold is evaporated before the growth of the a-Si layer, there is much less contact between gold and silicon atoms and very little stimulus for gold to diffuse into the interstitial sites of the a-Si layer. In contrast, when silicon is deposited onto the gold nanoparticles, the larger number of surface atoms and lower number of nearest neighbor gold atoms on the surface of the gold nanoparticles leads to the diffusion of gold atoms into the silicon lattice and the formation of a gold silicide. Moreover, the a-Si layer around the gold nanoparticle may have more defects than the a-Si on the flat substrate, which could enhance gold atom diffusion\textsuperscript{61,62}. Gold atom diffusion has been shown to be possible through very small openings\textsuperscript{63}. This aligns with the observation of Au 4f doublet shoulders in previous studies because gold films fabricated by vacuum evaporation onto a c-Si or a-Si substrates would lead to clustered Au atoms\textsuperscript{26,28} that exhibit chemical properties similar to nanoparticles. These clustered Au atoms would enhance silicide formation within contact with the Si layer before a continuous layer of Au-Au metallic bonds has the chance to be formed. The formation of a gold silicide alters the optical properties of the device, which needs to be taken into account or even exploited. The silicide formation process halts when a stoichiometric layer has been formed, which has a passivating effect around the gold nanoparticle. The dielectric properties of such a silicide layer can be included in the optical modelling of such a system. Moreover, because electron-hole recombination occurs often at the semiconductor-metal interface, this native silicide layer may reduce this surface recombination considerably, leading to improvements in solar cell efficiencies.

Conclusions

Many previous studies have investigated the formation of a gold silicide interface between thermally evaporated gold films of nanoparticles deposited on top of either a-Si or c-Si. Here, we have shown that gold nanoparticles embedded by a-Si as grown on top without any heat treatment, also leads to the formation of a silicide. The driving force behind the formation of an Au rich silicide is the nanostructure of the gold, making the individual gold atoms more likely to interact with the Si layer. The lower number of nearest neighbors at the surface of the nanoparticle, in addition to the affinity of gold for the dangling bonds of the a-Si layer, allows Au atoms at the surface to overcome Au-Au interactions and diffuse into the a-Si matrix. The higher concentration of defects in a-Si around the nanostructure enhances this effect. In contrast, the bulk gold film has a higher number of nearest neighbors, which inhibits the silicide formation. The TEM analysis shows that a high concentration but irregular/non-uniformly distributed
diffusion of Au into a-Si occurs as well, likely due to void or crack formation. High defect concentrations induced by the gold nanostructure or its intercalated atoms likely stimulate oxidation. The presence of the silicide at the interface between Au nanoparticles and the surrounding a-Si film has significant implications for engineering high efficiency novel concept solar cells and photodetectors that incorporate gold nanoparticles as plasmonic nanostructures.

**Supporting Information:** XPS: Approximating the thickness of a-Si on top of Au nanoparticles and determining whether charge accumulated on the a-Si/AuNP25nm sample after subsequent sputtering steps. HAADF TEM images of gold nanoparticles inside a-Si at different scales. STEM image of single gold particle inside a-Si with EELS and STEM EDX maps.

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