Engineered optical properties of silver-aluminum alloy nanoparticles embedded in SiON matrix for maximizing light confinement in plasmonic silicon solar cells

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Self-assembled silver-aluminum (Ag-Al) alloy nanoparticles (NPs) embedded in SiO₂, Si₃N₄, and SiON dielectric thin film matrices explored as a hybrid plasmonic structure for silicon solar cells to maximize light confinement. The Ag₂Al NPs prepared by ex-vacuo solid-state dewetting, and alloy formation confirmed by X-ray diffraction and photoelectron spectroscopy analysis. Nanoindentation by atomic force microscopy revealed better surface adhesion of alloy NPs on silicon surface than Ag NPs due to the Al presence. The SiON spacer layer/Ag₂Al NPs reduced silicon average reflectance from 22.7% to 9.2% due to surface plasmonic and antireflection effects. The SiON capping layer on NPs reduced silicon reflectance from 9.2% to 3.6% in wavelength region 300–1150 nm with preferential forward light scattering due to uniform Coulombic restoring force on NPs' surface. Minimum reflectance and parasitic absorbance from 35 nm SiON/Ag₂Al NPs/25 nm SiON structure reflected in plasmonic cell's photocurrent enhancement from 26.27 mA/cm² (of bare cell) to 34.61 mA/cm² due to the better photon management. Quantum efficiency analysis also showed photocurrent enhancement of cell in surface plasmon resonance and off-resonance regions of NPs. We also quantified dielectric thin film antireflection and alloy NPs plasmonic effects separately in cell photocurrent enhancement apart from hybrid plasmonic structure role.

The photon management in silicon (Si) solar cells is never ending quest, emerging nanophotonics/plasmonics ideas are also providing an alternate option for the light confinement/trapping in Si wafers apart from conventional light randomization techniques. For localized surface plasmon resonances (LSPRs) assisted light trapping (resonant light path enhancement) in Si solar cells, the metal nanostructures have been the choice. The selection of metal for plasmonics application depends on the dielectric constant (density of conduction band electrons plays a role) and interband transitions. For plasmonic silicon solar cells (PSSCs); the very common metal has been silver (Ag) due to favourable dielectric properties and material stability. But, the Ag nanoparticles (NPs) exhibited a reduction in photocurrent of PSSCs near the LSPR region due to the Fano resonance, and parasitic absorption losses after integrating on the front side of a silicon cell, and also the Ag NPs possess poor surface adhesion.

As an alternative low cost and abundant material, aluminum (Al) NPs are investigated as broadband plasmonic light scatterers for Si solar cells due to the weaker interband damping of dipolar LSPRs despite the difficulty in NPs formation. The Al also acts like Drude metal below and above the interband transition region, and also has the longer LSPRs dephasing time. The Al NPs support LSPRs in blue and UV regions of the light spectrum, which can diminish the possibility of the Fano resonance losses. In addition, the Al also exhibits large surface adhesion to a supporting substrate due to the larger shear stress, which may lead to undesired high surface coverage of NPs. However, surface oxidation of the Al NPs is a major issue; oxidized surface (shell layer) can also be exploited for better light forward scattering into the Si solar cells due to modification in the dielectric environment.
Metal nanocomposites like; core-shell and bimetallic/alloys possess unique physico-chemical properties (after tuning dielectric function) with different composition of metal at the nanoscale than their constituent metals. This approach can open up a broad range of applications in nanophotonics, biomedical, and also for energy harvesting14–18. For broad wavelength light forward scattering into a Si wafer and to avoid undesirable surface oxidation of the NPs, a dielectric matrix of lower refractive index medium than a Si was used for embedding the NPs (Si/spacer layer/metal NPs/capping layer)6,19,20. A thin dielectric spacer layer between the metal NPs and high index substrate can modulate the metal NP's near-field incoupling into a substrate due to graded refractive index medium18, and also can help in removing electronic trap states at the front surface of Si wafer to minimize the surface recombination21. Whereas a capping layer on metal NPs prevents surface oxidation4, and then the Fano resonance loss by influencing the polarization charges at the NP's surface19,22.

The SiO2 and Si3N4 are commonly adopted dielectric materials as spacer/capping layers for tuning the LSPR's fields of the metal NPs6–9. However; silicon oxynitride (SiON) film has the lower parasitic absorption losses, tunable refractive index medium5, low density of surface states, and has large energy band gap (5–9 eV); which makes the SiON film optically and electrically more promising than the conventional SiO2 and Si3N4 dielectric films24. Still, there is a scope for improving the light absorption in a weakly absorbing Si wafer by engineering front anti-reflection layer with the plasmonics concept by minimization of parasitic absorption, surface oxidation, and the Fano resonance losses. In this work, we try to investigate and exploit the positive effects of a hybrid plasmonic structure consisting of alloy metal NPs and complex dielectric layer for better photon management in silicon solar cells using the simple sputter deposition technique.

Results and Discussions

Structural Properties. Figure 1a shows the elemental composition of the Ag-Al NPs on a Si wafer, inset of figure shows detected elements weight percentage; the Al is 10.34 ± 1.20 wt. % of total metal composition. Figure 1b shows the XRD patterns of as-deposited Ag-10 wt. % Al thin film, and in the NPs form after annealing at 350 °C for 1 hour; the standard Al/Ag planes are also presented for reference. The diffraction peaks of Ag/Al at 38.17°, 44.34° and 64.45° are observed, which correspond to (111), (200) and (220) planes, respectively. A small diffraction peak also observed at ~32° from the as-deposited film, which is related to (100) plane of an intermetallic compound of the Ag2Al (δ-phase)17. After annealing, the intensity of the (100) peak enhanced, and an additional peak at ~62.42° related to the (110) plane also observed, which is evidence for the formation of δ-phase of Ag2Al alloy NPs18. The pure Ag/Al and δ-phase of Ag2Al have shown the intense (111) and (100) peaks, respectively, which is an indication of the good quality crystalline lattice in each of NPs grains. The Ag/Al crystal lattice parameter of (111) plane is 0.4082 nm, which is nearly same (0.4089 nm) as reported in literature15, whereas the Ag-Al crystal lattice parameter of (100) plane is 0.4811 nm.

Figure 1c signifies alteration in real and imaginary dielectric constants of the Ag2Al alloy NPs than the pure Ag NPs; the graphs are obtained after fitting the ellipsometry data using Gen-Osc model. The εreal of Ag2Al NPs has exhibited a small change at longer wavelength region, but a significant change in the εimag after 500 nm due to the interband transition (IT) region of Ag, in comparison to the Ag NPs. The IT region of the Ag is around 320 nm (between the d-like and sp-like bands near the L symmetry axis), whereas for the Al active IT region is ~820 nm (near the W point transition between a pair of parallel bands around the Σ axis on the Γ–K–W–X plane)12. The Al does not have any d-band for contributing to the valence band, so, the distortion in the Ag lattice occurs with the Al replacement, which can appear in the shift of L1 → L3 transition after the alloy formation can tailor the IT and LSPR positions in comparison to the pure Ag NPs. Thus, the alloying of Ag with Al can help to reduce the parasitic absorbance by the alloy NPs than the pure Ag NPs2,30.

The δ-phase of Ag2Al NPs is further explored by a complementary technique like XPS, which can provide essential information relating to the chemical bonding and oxidation states of the elements. Figure 2 shows core energy levels of the pure Ag NPs’ Ag 3d state, and the Ag2Al alloy NPs’ Ag 3d, Al 2p, O 1s states. The Ag 3d spectrum has shown two peaks related to the Ag 3d5/2 and Ag 3d3/2 core energy levels (due to the spin–orbit coupling), whose binding energies (B. E.) are 368.2 ± 0.1 eV and 374.2 ± 0.1 eV, respectively (Fig. 2a). The B. E. values are in good agreement with the reported Ag NPs19, as well as with the bulk Ag27. The Ag2Al NPs’ Ag 3d5/2 and 3d3/2 core energy levels are 368.7 ± 0.1 eV and 374.7 ± 0.1 eV, respectively, which are slightly larger (+0.5 eV) than the pure Ag NPs (Fig. 2a). The shoulders are also observed at lower energy side, which suggests the existence of Ag+ oxidic
state (Ag2O)\textsuperscript{16,27}. The Al 2p spectrum (Fig. 2c) has shown two peaks; one at 73.4 ± 0.1 eV related to metallic Al 2p (Al\textsuperscript{0}) core level, and another one at 75.9 ± 0.1 eV related to the Al\textsuperscript{3+} state of Al\textsubscript{2}O\textsubscript{3} phase\textsuperscript{28}. In O 1 s spectrum (Fig. 2d), we have observed three peaks at 528.7 ± 0.1 eV, 531.8 ± 0.1 eV and 530.2 ± 0.1 eV energy positions, which are of oxygen in Ag\textsubscript{2}O, AgO, and Al\textsubscript{2}O\textsubscript{3} phases, respectively, a small peak ~532.3 ± 0.1 eV relating to the adsorbed water is also observed\textsuperscript{29}.

Our main observation from the XPS data is; the core energy levels of Ag (Fig. 2a) appeared slightly at the higher binding energy than those reported in the literature\textsuperscript{25}. This variation can be attributed to difficulties in interpreting X-ray emission from the metals, where the 'd' energy bands lie a few electronvolts just below the Fermi energy level. The core energy level peaks exhibited a shift to the higher energy side upon alloying the Ag NPs (Fig. 2b), which indicates the decrease of electron density at an atomic site in comparison to simple ionic compounds\textsuperscript{16,28}. This B. E. shift can also the partial coverage of surfaces by chemisorbed species or oxides that can change the electronic environment around the Ag atoms. Also, the narrower photoemission spectra of the alloy NPs' d-bands (of the Ag) are observed in comparison to the pure Ag (Fig. 2b). With the Al presence in Ag matrix, the reactivity with oxygen is observed (Fig. 2b–d), but does not appear in the XRD pattern (Fig. 1b). Yang et al. only observed the Al\textsubscript{2}O\textsubscript{3} signature in the XRD spectrum after >20 wt. % of Al in the Al-Ag alloy thin films\textsuperscript{17}.

It is essential to understand how the NPs adhere to a substrate for integrating on a device structure. The cohesion between the substrate and discontinuous metal film will affect the NPs’ morphology (size, shape, and coverage) while minimizing the energy of the system during the NPs preparation (dewetting process). The NPs’ adhesion on a Si substrate can be analyzed by the shear stress (\(\tau_{\text{max}}\)) estimation (it is a function of Young's modulus E), which we have obtained from the force curves (based on sample-tip interactions) after the AFM indentation. Figure 3a and b show the force versus distance (piezo 'z' position) curves for the Ag and Ag\textsubscript{2}Al NPs, respectively. Here, the Si tip (Poisson ratio \(= 0.3\) and spring constant \(= 42\, \text{N.m}^{-1}\)) is used for indentation instead of the diamond coated tip (for hardness measurements). Retraced force curves are analyzed by the Nanoscope software (Derjaguin-Muller-Toporov fit model) for the NPs’ Young modulus estimation; the fit model assumes the contact profile remains the same as in the Hertzian model with inclusion of an adhesion force\textsuperscript{30}. From the Fig. 3b, one can observe the larger downward piezo deflection for the alloy Ag\textsubscript{2}Al NPs than the pure Ag NPs, which revealed the more adhesive force between the tip and Ag\textsubscript{2}Al NPs, which is an indication of the better adhesion of the alloy NPs to a Si surface.

To support the above statement, we also estimated \(\tau_{\text{max}}\) values using following relation and presented in the Fig. 3c. The \(\tau_{\text{max}}\) of the system can be written in an elastic regime as\textsuperscript{31}.

\[ \tau_{\text{max}} = \frac{1}{2} F \times \frac{d}{2} \]
where the $P_{\text{max}}$ is peak load applied to a cantilever, the $E_s$ and $\nu_s$ are Young's modulus and Poisson's ratio of the sample, respectively. The Poisson's ratio of the Ag and Al alloy are 0.37, and 0.32, respectively. The 'E' values are obtained from the force curves (Nanoscope analysis), for the Ag NPs and Ag$_2$Al NPs the values are 83.2 GPa and 109.7 GPa, respectively. The estimated shear stress ($\tau_{\text{max}}$) values of the Ag NPs and Ag$_2$Al NPs are 0.089 MPa and 0.2 MPa, respectively; the alloy Ag$_2$Al NPs adhesion is more than twice the pure Ag NPs adhesion on the silicon surface. Further, the work function of Ag$_2$Al alloy NPs are also investigated by the KPFM (Kelvin Probe Force Microscopy) and compared with the pure Ag NPs, related to this discussion is presented in the supplementary information (Fig. S1).

**Surface Morphology of Ag$_2$Al alloy nanoparticles.** Figure 4a–c show SEM micrographs of the Ag$_2$Al NPs (surface morphology and NPs' size distribution) embedded in 70 nm SiO$_2$, 50 nm Si$_3$N$_4$, and 60 nm SiON thin films matrix on the textured Si wafers. The alloy NPs embedded in the SiO$_2$ film (Fig. 4a) has shown average particles size distribution of ~60 and ~120 nm (for the NPs' average size estimation the area weighted mean diameter is used). The NPs in the Si$_3$N$_4$ film has shown average size of ~135 nm with the more surface coverage (Fig. 4b). Whereas the alloy NPs embedded in the SiON film has shown average size of ~115 nm (Fig. 4c), the size distribution is in Gaussian shape that suggests the minimum size deviation.

The NPs formation by the solid-state dewetting process has driven by the substrate and metal film surface energies difference, which breaks the metal film into nanoislands. In this process; the supporting substrate/film surface roughness and metal film's thermal conductivity are important parameters, which can affect the diffusion and merger of small metal clusters at growth sites during the NPs formation. The measured surface roughness is nearly same (~0.34 ± 0.11 nm) for all three dielectric films, so, which is not going to play any critical role in the NPs formation. Thus, the thermal conductivity of the dielectric film can play a crucial role in the variation of NPs growth; the minimum thermal conductivity of SiO$_2$ (1.3 W/m-K) led to two different NPs' size distribution, whereas the maximum value of Si$_3$N$_4$ (20 W/m-K) led to the single size distribution. Whereas the SiON film thermal conductivity is ~12 W/m-K, this intermediate value led to the more uniform Ag$_2$Al alloy NPs with sizes distribution between 90 to 140 nm.
Optical Properties. Figure 5a–c show total reflectance from the T-Si surface after integrating plasmonic hybrid structure (Ag₂Al NPs embedded in SiO₂, Si₃N₄, and SiON thin film matrices) in the wavelength range from 300 to 1150 nm. The average light reflectance from the bare T-Si wafer is ~22.7%, which is considered as a reference. To select a suitable dielectric matrix thickness for the alloy metal NPs integration on a T-Si surface for maximum reflectance reduction, the quarter-wavelength law of destructive interference (near NPs’ LSPR region of 400 to 410 nm) is adopted. The refractive indices of SiO₂, Si₃N₄ and SiON are 1.48, 1.97 and 1.7, respectively. From the quarter-wavelength law \( t = \frac{\lambda}{4n} \) (where \( t \) is the thickness of the dielectric layer, \( \lambda \) is the wavelength of incident light, and \( n \) is the refractive index of the dielectric layer), the SiO₂, Si₃N₄ and SiON layers thicknesses are ~70 nm, ~50 nm and ~60 nm, respectively. First, with ~40 nm SiO₂, ~30 nm Si₃N₄ and ~35 nm SiON spacer layer thicknesses, the average reflectance from the Si wafer reduced to ~14.5%. After the Ag₂Al NPs integration on 40 nm SiO₂, 30 nm Si₃N₄ and 35 nm SiON spacer layers reflectance reduced to 10.5%, 13.8%, and 9.2%, respectively. Finally, with 30 nm SiO₂, 20 nm Si₃N₄ and 25 nm SiON capping layers on the Ag₂Al NPs, the reflectance further reduced to ~7.2%, ~6.8%, and ~3.6%, respectively. From the above observations, the average layer thickness of ~60 nm of any dielectric layer still can provide the light trapping. However, one needs to consider the effect of spacer layer thickness for different dielectric matrices, which is very sensitive to the metal NPs’ surface plasmon mode induced near-fields coupling into the Si. Further, reflectance spectra of hybrid plasmonic structures normalized to a reference bare T-Si surface are also presented in the supplementary information (Fig. S2).

The Ag₂Al alloy NPs on the SiO₂ and SiON spacer layers led to the reflectance reduction in the surface plasmon resonance region. Whereas, with the Si₃N₄ spacer layer, slight increase in reflectance in resonance region and a small decrease in reflectance in the off-resonance region (Fig. 5b). The spacer layer can reduce the refractive index gradient between the silicon and air, which can break the symmetry of polarization of the NPs that can lead to the preferential incoupling of the plasmon-induced field with more intensity into the Si wafer. But, the spacer layer also influences the growth of NPs (Fig. 4), which can affect the light interaction by two ways; (i) the small size NPs can increase the parasitic absorption, and (ii) the destructive interference (hybridization of LSPR modes) due to large coverage/size of the NPs.

After the capping layers integration, the Ag₂Al alloy NPs led to the reflectance reduction in both surface plasmon resonance and off-resonance region of the NPs. The light-NPs interaction at the nanoscale is very sensitive to the physical environment of NPs besides NPs’ size and shape. A capping layer can provide homogeneous dielectric environment around the NPs, which can enhance the alloy NPs’ near-field intensity by minimizing the SPRs dephasing losses. The reflectance reduction in the entire polychromatic spectral region is due to the effective NPs’ near fields coupling with the sandwich structure instead of just the spacer layer, which is led by the broad angle light forward scattering in all wavelengths. In the case of large size NPs, the capping layer is also required for reducing phase mismatch between the incident and scattered light fields (back scattering due to the
Fano resonance losses) in the LSPR region (Fig. 5b), which further improves the light forward scattering. The hybrid plasmonic structure of 35 nm SiON/Ag2Al NPs/25 nm SiON provided the high density of optical modes, which led to an increase in absorption in the silicon wafer with the minimum average reflectance of ~3.6% in 300 to 1150 nm wavelength region (Fig. 5c). One should also know parasitic absorptance losses by the metal NPs, to estimate the effective absorption efficiency of the silicon wafer for the photo-conversion. Figure 5d shows absorptance of the plasmonic structure (on the glass) comprised of alloy NPs embedded in the dielectric medium. The absorptance is estimated using the relation:

\[ \text{A} = 100 - \frac{\text{T}_{\text{tot}}}{\text{R}_{\text{tot}}} \]

where \( \text{T}_{\text{tot}} \) and \( \text{R}_{\text{tot}} \) are the total transmittance and total reflectance of alloy NPs deposited on a glass substrate, respectively. Average absorptance of the Ag2Al NPs embedded in the SiO2, Si3N4, and SiON films is ~5.8%, ~6.8%, and ~4.6%, respectively, in the spectral region of 300 to 1150 nm. In the LSPR region, the absorptance is maximum due to the parasitic absorption by the NPs. The minimum loss with the SiON film can be either based on the extinction of dielectric material itself or slight variation in the size/density of the NPs. To confirm the plasmonic effect and the superiority of alloy NPs over pure metal NPs, theoretical modeling is required. The elementary theoretical analysis using a finite-element method of alloy NPs’ scattered light into the silicon wafer, and angular/spatial distribution of NPs’ far-fields at the Si/Ag2Al NP interface is presented in the supplementary material.

### Electrical Properties

To investigate the photo-conversion, we integrated the hybrid plasmonic structure on the conventional textured Si solar cells. Figure 6a shows the J-V graphs of bare Si solar cell (C1), C1 with ~60 nm SiON dielectric film only, C1 with Ag2Al NPs only, and C1 with optimized hybrid plasmonic structure (35 nm SiON/Ag2Al NPs/25 nm SiON); the corresponding photovoltaic parameters are also summarized in Table 1. The statistical variation of the cells’ short-circuit current (Jsc), open circuit voltage (Voc), Fill Factor (FF), and power conversion efficiency (\( \eta \)) are also presented in the supplementary information (Fig. S3). The bare cell C1 has shown \( J_{\text{sc}} \) of 26.27 mA/cm², \( V_{\text{oc}} \) of 594.76 mV, FF of 69.40, and \( \eta \) of 10.82%. With the plasmonic hybrid structure, the \( J_{\text{sc}} \) (from 26.27 to 34.61 mA/cm²) and \( \eta \) (from 10.82% to 15.04%) of the cell enhanced impressively in comparison to the bare cell C1.

There is a consistent \( J_{\text{sc}} \) enhancement from cells with different configurations in comparison to the bare cell C1; (a) C1/35 nm SiON is 13.58% (from 26.27 to 29.84 mA/cm²), (b) C1/60 nm SiON is 16.37% (from 26.27 to 30.57 mA/cm²), (c) C1/35 nm SiON/Ag2Al NPs is 28.36% (from 26.27 to 33.72 mA/cm²), (d) C1/Ag2Al NPs is 9.4% (from 26.27 to 28.74 mA/cm²), and (e) C1/35 nm SiON/Ag2Al NPs/25 nm SiON is 31.74% (from 26.27 to

![Image of J-V graphs and EQE spectra](image-url)

**Figure 6.** (a) J-V graphs, and (b) EQE spectra of the bare cell (C1), C1/35 nm of SiON spacer layer, C1/35 nm of SiON/Ag2Al NPs, C1/35 nm of SiON/Ag2Al NPs/25 nm SiON capping layer, C1/60 nm SiON, and C1/Ag2Al NPs. Inset of the EQE spectra shows schematic of PSSC.

| Device                  | Jsc (mA/cm²) | Voc (mV) | FF   | \( \eta \) (%) |
|-------------------------|--------------|----------|------|---------------|
| Bare Cell (C1)          | 26.27        | 594.76   | 69.40| 10.82         |
| C1/35 nm SiON           | 29.84        | 595.20   | 71.59| 12.81         |
| C1/35 nm SiON/Ag2Al NPs| 33.72        | 599.41   | 72.51| 14.58         |
| C1/35 nm SiON/Ag2Al NPs/25 nm SiON | 34.61 | 601.03 | 72.44 | 15.04       |
| C1/60 nm SiON           | 30.57        | 596.43   | 72.17| 13.15         |
| C1/Ag2Al NPs            | 28.74        | 598.18   | 72.05| 12.38         |

Table 1. Photovoltaic parameters of solar cells; bare cell (C1), C1/35 nm of SiON spacer layer, C1/35 nm of SiON/Ag2Al NPs, C1/35 nm of SiON/Ag2Al NPs/25 nm SiON capping layer, C1/60 nm SiON, and C1/Ag2Al NPs.
multi-crystalline solar cell photocurrent enhancement with 60 nm Au NPs embedded in SiNₓ matrix, which in the off-resonance region (600–1000 nm) of the NPs enhanced in comparison to the bare cell, which is due to also have observed a very small parasitic absorption by the alloy NPs (Fig. 5d). However, the device photocurrent of SiON spacer layer, C1/35 nm of SiON/Ag₂Al NPs, C1/35 nm of SiON/Ag₂Al NPs/25 nm SiON capping layer, C1/60 nm SiON, and C1/Ag₂Al NPs. With 35 nm SiON spacer layer, the photocurrent of the device improved mainly in 300–500 nm wavelength region due to an anti-reflection effect. After the Ag₂Al NPs integration on 35 nm SiON film, a small reduction in photocurrent near the LSPR region (~410 nm) despite reduced reflectance (Fig. 5c), which is due to parasitic absorption by the NPs (Fig. 5d). The metal nanostructures absorb the incident light along with the light scattering, the absorption/scattering is very sensitive to the metal nanoparticles’ morphology. The parasitic absorption of light by the NPs will not contribute to the carrier generation near the incident light along with the light scattering, the absorption/scattering is very sensitive to the metal nanoparticles’ morphology. The parasitic absorption of light by the NPs will not contribute to the carrier generation near the LSPR region (Fig. 6b). Usually, the parasitic absorption is very small in large size (>100 nm) metal NPs, we also have observed a very small parasitic absorption by the alloy NPs (Fig. 5d). However, the device photocurrent in the off-resonance region (600–1000 nm) of the NPs enhanced in comparison to the bare cell, which is due to the preferential light forward scattering by the alloy NPs’ dipole-dipole and/or dipole-quadrupole fields.

With the 25 nm SiON capping layer, the net positive effect in photocurrent enhancement is observed in the polychromatic spectral range region (300 to 1100 nm wavelength region). Fahim et al. also reported the textured multi-crystalline solar cell photocurrent enhancement with 60 nm Au NPs embedded in SiNₓ matrix, which attributed to the enhancement in light forward scattering and near-field by the NPs 19. With 60 nm thin SiON layer alone, the EQE of the cell is improved due to the standard antireflection effect, but smaller than the hybrid plasmonic structure. The cell C1 with the Ag₂Al NPs only has shown less improvement in the Jsc due to unfavourable light forward scattering from the NPs due to the large dielectric environment variation, and can also to some extent charge carrier trap states at the Si/NPs interface. The quantum efficiency analysis also proved the hybrid plasmonic structure role in an increase in light transmission through the silicon wafer by an enhancement in the photocurrent of the silicon solar cell.

### Conclusions

The Ag₂Al alloy NPs (Ag-10 wt. % Al) are embedded in the dielectric matrix for minimizing the optical losses from a silicon wafer. The light interaction with the 35 nm SiON/Ag₂Al NPs/25 nm SiON hybrid plasmonic structure reduced the reflectance of the textured silicon wafer from 22.7% to ~3.6% along with minimal parasitic absorption loss in the wavelength region 300 to 1150 nm. Reduced reflectance with the hybrid plasmonic structure led to the overall photocurrent improvement of the plasmonic cell is from 26.27 to 34.61 mA-cm⁻² and cell efficiency from 10.82% to 15.04% in comparison to bare silicon cell. This work demonstrated the hybrid plasmonic structure role by combining the dielectric thin film anti-reflection effects and alloy NPs’ high density of optical modes for the light confinement, to reduce the net optical loss in the textured silicon wafer and further on the silicon solar cell performance.

### Experimental Methods

#### Fabrication of alloy NPs in dielectric matrix.

The Ag-10 wt. % Al alloy NPs, and dielectric films of different thicknesses are deposited on p-type (100) oriented textured silicon (T-Si) of 180 ± 20 μm thickness and also on glass substrates by Radio Frequency (RF) magnetron sputtering system. The system working pressure was ~1.3 × 10⁻² mbar for all depositions. Before the deposition, the glass substrates cleaned ultrasonically in de-ionize water, acetone, and isopropyl alcohol sequentially; the T-Si wafers cleaned by the standard Radio Corporation of America method followed by a native oxide removal in 5% hydrofluoric acid. The Ag-10 wt. % Al thin films of mass thickness 12 ± 0.2 nm co-sputtered, and subsequently annealed for 1 h at 350 °C in the N₂ ambient to form self-assembled NP arrays. The alloy film deposition calibrated to have desired chemical composition with 30 W and 10 W RF power for Ag and Al metals, respectively. To embed the alloy NPs in a dielectric matrix, first dielectric spacer layer sputtered on the T-Si wafer, afterwards, the Ag₂Al NPs prepared on the spacer layer, and again, the same dielectric film deposited on the alloy NPs as a capping layer. Silicon dioxide (SiO₂), silicon nitride (Si₃N₄), and silicon oxynitride (SiON) films used as dielectric matrices (thickness details of the spacer and capping layers provided in Table 2). The SiO₂ and Si₃N₄ films deposited with 120 W and 75 W RF power, respectively; for the SiON films deposition by co-sputtered with the same RF power applied for the SiO₂ and Si₃N₄ targets.

| Sr. No. | Dielectric material | Spacer layer thickness (nm) | Capping layer thickness (nm) |
|---------|---------------------|-----------------------------|-----------------------------|
| 1.      | SiO₂                | 40                          | 30                          |
| 2.      | Si₃N₄              | 30                          | 20                          |
| 3.      | SiON                | 35                          | 25                          |

Table 2. Thickness of spacer and capping layers in which the Ag₂Al NPs embedded.

34.61 mA-cm⁻²). The enhancement in photocurrent of the cell is due to the plasmonic effects from the NPs and antireflection effects from thin dielectric films. The better performance of PSSCs primarily by the alloy NPs’ near fields coupling via spacer/capping layers, and further light effective scattering into the silicon wafer 20. However, the enhancement of η (39.0%) is larger than the enhancement η (31.74%), which is due to the improvement in Voc (from 594.76 to 601.03 mV) and FF (from 69.40 to 72.44). The modification in Voc and FF is primarily due to the improvement in surface passivation by the spacer layer that can reduce the series resistance of the plasmonic device 8.

The quantum efficiency analysis can also provide the better understanding of optical-to-electrical conversion efficiency in surface plasmon resonance and off-resonance regions of the NPs that cumulatively influence the Jsc of PSSCs (Fig. 6a). The EQE spectra of all cells are presented in Fig. 6b, which elucidate the incident photon to current conversion efficiency modification as a function of the wavelength for the bare cell (C1), C1/35 nm of SiON spacer layer, C1/35 nm of SiON/Ag₂Al NPs, C1/35 nm of SiON/Ag₂Al NPs/25 nm SiON capping layer, C1/60 nm SiON, and C1/Ag₂Al NPs. With 35 nm SiON spacer layer, the photocurrent of the device improved mainly in 300–500 nm wavelength region due to an anti-reflection effect. After the Ag₂Al NPs integration on 35 nm SiON film, a small reduction in photocurrent near the LSPR region (~410 nm) despite reduced reflectance (Fig. 5c), which is due to parasitic absorption by the NPs (Fig. 5d). The metal nanostructures absorb the incident light along with the light scattering, the absorption/scattering is very sensitive to the metal nanoparticles’ morphology. The parasitic absorption of light by the NPs will not contribute to the carrier generation near the LSPR region (Fig. 6b). Usually, the parasitic absorption is very small in large size (>100 nm) metal NPs, we also have observed a very small parasitic absorption by the alloy NPs (Fig. 5d). However, the device photocurrent in the off-resonance region (600–1000 nm) of the NPs enhanced in comparison to the bare cell, which is due to the preferential light forward scattering by the alloy NPs’ dipole-dipole and/or dipole-quadrupole fields.

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### Experimental Methods

#### Fabrication of alloy NPs in dielectric matrix.

The Ag-10 wt. % Al alloy NPs, and dielectric films of different thicknesses are deposited on p-type (100) oriented textured silicon (T-Si) of 180 ± 20 μm thickness and also on glass substrates by Radio Frequency (RF) magnetron sputtering system. The system working pressure was ~1.3 × 10⁻² mbar for all depositions. Before the deposition, the glass substrates cleaned ultrasonically in de-ionize water, acetone, and isopropyl alcohol sequentially; the T-Si wafers cleaned by the standard Radio Corporation of America method followed by a native oxide removal in 5% hydrofluoric acid. The Ag-10 wt. % Al thin films of mass thickness 12 ± 0.2 nm co-sputtered, and subsequently annealed for 1 h at 350 °C in the N₂ ambient to form self-assembled NP arrays. The alloy film deposition calibrated to have desired chemical composition with 30 W and 10 W RF power for Ag and Al metals, respectively. To embed the alloy NPs in a dielectric matrix, first dielectric spacer layer sputtered on the T-Si wafer, afterwards, the Ag₂Al NPs prepared on the spacer layer, and again, the same dielectric film deposited on the alloy NPs as a capping layer. Silicon dioxide (SiO₂), silicon nitride (Si₃N₄), and silicon oxynitride (SiON) films used as dielectric matrices (thickness details of the spacer and capping layers provided in Table 2). The SiO₂ and Si₃N₄ films deposited with 120 W and 75 W RF power, respectively; for the SiON films deposition by co-sputtered with the same RF power applied for the SiO₂ and Si₃N₄ targets.
Device Fabrication. Optimized hybrid plasmonic layer (35 nm SiON/Ag-Al alloy NPs/25 nm SiON) is integrated on the conventional crystalline textured Si solar cells. For a cell fabrication, p-type Czochralski wafer (resistivity of 1–5 Ω-cm) used as a base, a shallow ~0.3 μm n-type layer has grown on the wafer by POCl3 diffusion at ~820 °C for 40 min. Silver and aluminum materials are sputtered on the front and rear sides of a p-n junction, respectively; followed by co-firing for 5 s at ~800 °C to form the Ohmic contacts on both sides of the p-n junction. The standard SiNα anti-reflection coating (ARC) step avoided, to investigate the hybrid plasmonic layer effect on the cell performance.

Characterizations. Energy Dispersive X-ray spectroscopy (EDX) analysis carried out for the alloy composition estimation. The structural and phase analysis of Ag-Al alloy NPs conducted by X-Ray Diffraction (XRD; Rigaku Ultima IV) technique with the Cu Kα source (λCuKα = 1.5406 Å). The optical constants of Ag-Al alloy NPs estimated by a variable angle spectroscopic ellipsometer (VASE, J. A. Woollam M-2000) in 300–1100 nm wavelength region. The chemical and oxidation states of Ag and Al in the Ag-Al NPs determined by X-ray Photoelectron Spectroscopy (XPS) using the Mg Kα (1253.6 eV) source. For nanoindentation, the AFM (Bruker, Dimension Icon) employed to estimate the elastic modulus (from shear stress analysis), and work function analysis by KPFM of the alloy NPs. Surface topology of self-assembled Ag-Al NP arrays analyzed by Scanning Electron Microscope (SEM, Carl Zeiss EVO-50). Optical measurements performed by Perkin-Elmer Lambda 1050 UV-Vis-NIR spectrophotometer with an attachment of 150 mm integrating sphere in 300–1100 nm wavelength region. The plasmonic solar cell’s current-density-voltage (J-V) characteristics recorded using Class AAA solar simulator (Oriel Sol3A, Newport, USA). External Quantum Efficiency (EQE) spectra recorded using quantum efficiency measurement system (SPEQuest, ReRa Solutions, The Netherlands) with AM 1.5 G incident solar spectrum.

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**Author Contributions**
P.K.P. conducted all the experimental works. P.K.P. and V.K.K. wrote the manuscript and assisted the interpretation of measurement data.

**Additional Information**

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