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Shifting the aluminum nanoparticle plasmon resonance to the visible with SiN and a-Si thin films

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ABSTRACT

Metal nanoparticles have strong optical resonances, which can be used to enhance optical absorption, particularly in thin film solar cells. Most research on these plasmon resonances in the context of solar cells has been performed on gold and silver nanoparticles. As these materials are expensive, alternatives are needed. Aluminum nanoparticles have a plasmon resonance in the UV, but by embedding these particles in silicon nitride or amorphous silicon, the plasmon resonance can be shifted to the visible part of the spectrum. Using a gas aggregation cluster source for the particles and magnetron sputtering for the thin films, aluminum nanoparticles were embedded in silicon nitride and amorphous silicon thin films, which shifted the optical resonance of the metal nanoparticles. The optical absorption of particles embedded in amorphous silicon was not at the expected wavelength, but the results of particles embedded in silicon nitride were in good agreement with FDTD simulations. This work is a next step for cheap plasmonics in solar cells

1. Introduction

Using plasmonic nanostructures in solar cells could contribute to enhanced absorption in the active layer and thereby increase the solar cell efficiency. This can be achieved by the local field enhancement and scattering of plasmonic nanostructures [1–4]. To date, most research focused on noble metals [5,6], which have strong resonances in the visible part of the spectrum and have the advantage of being inert. However, the high price of noble metals makes them unsuitable for commercial solar cells. Although aluminum has its bulk plasmon resonance in the far UV around 150 nm, its plasmon resonance can be shifted, making it a cheap alternative. The plasmon resonance wavelength of aluminum nanoparticles can be shifted towards the visible by selection of size, shape, and configuration [7–12]. This plasmon resonance shift makes the aluminum particles suitable for solar cells. The electron collision frequency at a plasma frequency in the visible in aluminum is in between that of gold and silver [13], which make Ohmic losses acceptable. A theoretical study by Akimov at al. [14] has demonstrated that aluminum particles increases the optical absorption in a-Si:H over a wide wavelength range, better than silver particles. However, light management by plasmonic nanostructures is mainly interesting for thin film solar cells since they have significant transmittance. This thin thickness also restricts the size of the nanoparticles to about 30 nm. When using such small aluminum particles, oxidation can significantly reduce the aluminum metal size or even completely oxidize it. Therefore, covering the small aluminum particles with a protective layer is desirable.

In this work, the plasmon resonance frequency of small aluminum particles is shifted by embedding in a high refractive index dielectric matrix [15]. The polarizability of free electrons, which are on the surface of a metal, is affected by the polarizability of the surrounding medium. Compared to vacuum, with a surrounding dielectric medium, the electrons move slower, hence the shift towards the red. The use of small aluminum particles for solar cells has so far been limited due to strong oxidation, which in this method is prevented as there is no exposure to the ambient during fabrication. The optical absorption of aluminum particles embedded in a-Si and SiN provides clues to the changed plasmonic behavior of these nanoparticles.

2. Experimental

The aluminum nanoparticles were produced by a gas aggregation cluster source (Oxford Applied Research NF-200B [16,17]). The aluminum particles were deposited on glass samples of 1 cm^2 and 2–3 mm thick. The schematic picture is shown in Fig. 1A. High purity Argon gas was used for the plasma to sputter an Aluminum target of 99.99% purity. The glass slide with Aluminum particles was directly moved, continuously in vacuum, to a separate chamber for sputter deposition of a 25 nm thick amorphous silicon or a silicon nitride film. This small thickness ensures that no interference effects can occur above about 200 nm. Considering that the samples were in vacuum ($<10^{-5}$ mbar) during the

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depositions and the short transit time, the particles were not oxidized during this process. Only by exposure to air on purpose for several minutes, the aluminum particles became oxidized before deposition of the cover layer. It is estimated that a layer of 2–5 nm of oxide is formed [14]. This provided a method to inspect the difference between the metal (plasmonic) and (partially) oxidized particle. Aluminum particles were also deposited on a SiN TEM grid, for transmission electron microscopy inspection (Fig. 1B).

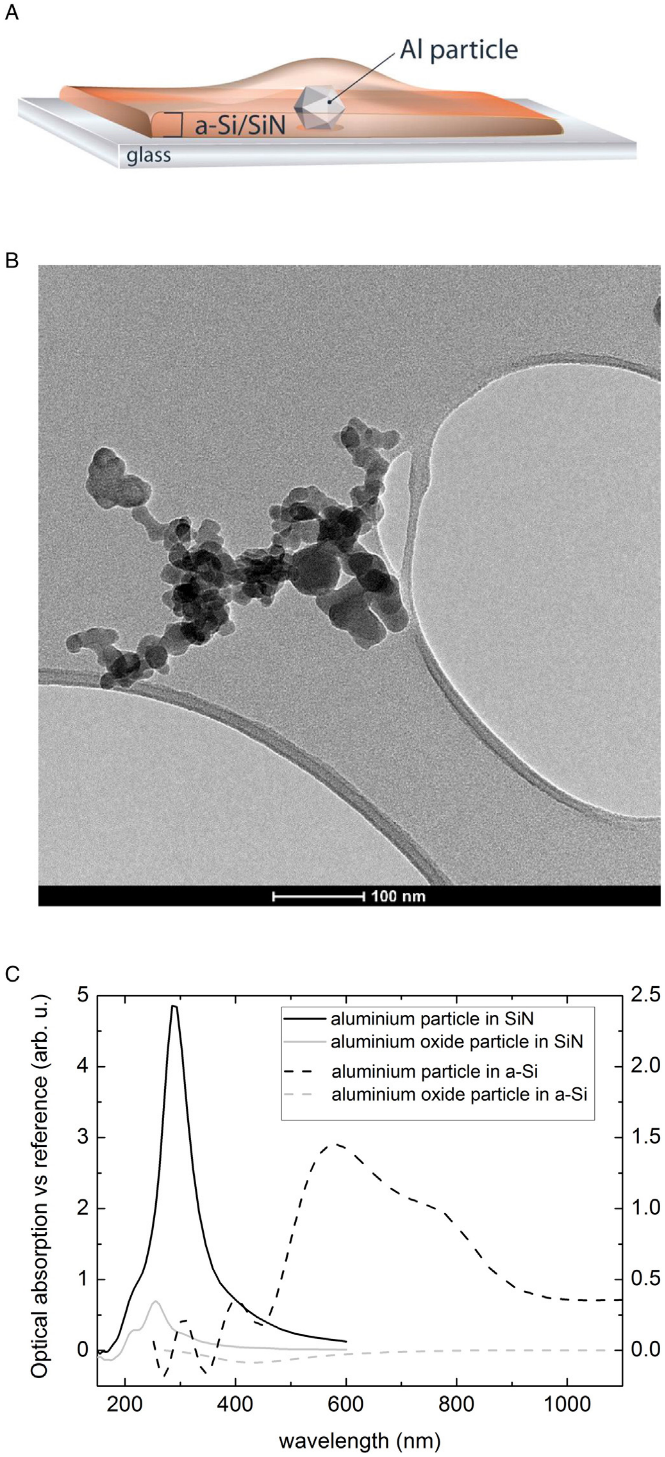

Fig. 1. (A) Schematic depiction of aluminum particles on glass with cover layer. (B) TEM image of aluminum particles, they are merged and oxidized. (C) Simulated optical absorption of aluminum (black) and aluminum particles with an oxide shell (gray) embedded in Si_3N_4 (solid) and a-Si (dashed, right axis).

The particle size and density were inspected with atomic force microscopy (AFM), while the film thickness was determined using the Bruker XT DEKTAK profilometer. The optical absorption measurements were performed with an Agilent Cary 5000 UV–VIS-NIR Spectroscope. The optical absorption spectra of films with particles were compared with films without particles by subtraction. The absorption was calculated by the difference between the reflection and transmission with unity. If the reflection or transmission has a too high value, caused by the limited sensitivity of the setup, the calculated absorption difference can become negative. However, the absorption difference should be positive as the plasmonic aluminium particles can only absorb more light at the plasmon resonance wavelength. Since the spectral properties of the reflection, absorption and transmission are connected through the plasmon resonance the negative value has to be multiplied by −1 to obtain an indication of the proper absorption difference. This method gives a good result for the wavelength dependence of the absorption but only gives an indication of the magnitude of the absorption.

Finite differential time domain (FDTD) simulations were performed with commercial software (Lumerical Solutions, Inc) on spherical particles on glass embedded in a conformal film. A total field scattered field source was used to determine the scattering and absorption cross sections. Convergence was tested for mesh size, simulation setup and boundary layers, which resulted in a 1 or a 1.5 nm mesh size. Pulse lengths are in the order of 2–8 fs. This source is a total field scattered field source which only lets scattered light through its boundaries. This way a field monitor around the source can be used to calculate the scattering cross section of the particle. The boundary conditions are perfectly matched layers (PML), which absorb all the incoming radiation.

3. Results and discussion

The FDTD simulations on aluminum (14 nm) and core (8 nm)-shell (4 nm) aluminum-oxide particles embedded in SiN and a-Si show in Fig. 1C that clear plasmonic resonances are visible at different wavelengths. Aluminum particles of 20 nm size have a plasmon resonance of at about 200 nm (6.2 eV) [7]. The shift of the plasmon resonance to 300 nm (4.1 eV) for SiN and 600 nm (2.1 eV) for a-Si is much larger as compared with plasmon resonance shifts of silver particles in glass and TiO2 [18].

When the particle contains an oxide shell, the plasmon resonance in SiN shifts slightly to 260 nm, which is explained by the lower value of the oxide refractive index around the metal core as compared to an un-oxidized particle. For the particle with oxide shell in a-Si, the plasmon oscillation loses considerable strength and is barely visible, which is likely the result of interband transitions, which are known to dampen plasmon strength [15]. Clearly, the value of the dielectric medium has a strong effect in this wavelength range, which is the onset of an interband transition at 1.4 eV [19]. At a wavelength range between 200 and 600 nm, the value is negative, which indicates that the oxidized aluminum particles transmit or reflect more light. Due to a difference in the absorption coefficient, the plasmonically enhanced local field around the aluminum core will become less absorbed in the aluminum oxide than in a-Si.

The experimentally fabricated aluminum particles embedded in a matrix are investigated with AFM as shown in Fig. 2. The individual particles are visible through the SiN and a-Si cover layer. The lateral features are different because of the tip convolution which differs often per scan. The height of the particles is a measure of their size (plotted in the insets) and has a wide distribution around about 8 nm, depending slightly on each deposition. Considering the conformal growth of the cover layer (matrix) this is a good estimate of the aluminum particle size.

Although the particle density is low, optical absorption spectroscopy provides a measurable effect of the aluminum and oxidized aluminum particles in the order of 1% as shown in Fig. 3. This is also in agreement