SILVER-NANOPARTICLE-BASED ETCH MASK CONTROL FOR SUBWAVELENGTH STRUCTURE DEVELOPMENT

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In this paper, we investigate the impact of silver thin film thickness and annealing temperatures for the fabrication of silver nano-particles of controlled size and spacing distributions. We also use these measured distributions to predict the performance of subwavelength grating structures developed using dry and isotropic etching of semiconductor substrates. Silver (Ag) thin films of different thicknesses were deposited on Si and GaAs semiconductor substrates and annealed at different temperatures. Experimental results demonstrate that by annealing the Ag thin films with different temperature profiles it is feasible to develop Ag nanoparticles of an average diameter ranging from 50 nm to 400 nm on silicon substrates and 100 nm to 500 nm on GaAs substrates.

In addition, different subwavelength structures developed by etching the Ag nanoparticle deposited Si and GaAs substrates are simulated using a Finite-Difference Time Domain (FDTD) software package. Simulation results show that substantial reduction in light reflection can be achieved by optimizing the heights of the subwavelength structures through the control of the etching process time.

Keywords: Subwavelength gratings (SWG), nanoparticles, nano-structures, solar cells, reflection loss, Finite Difference Time Domain (FDTD) simulation.

1. Introduction

Multilayered thin film coatings have been used extensively in a wide range of applications to realize antireflection (AR) properties that suppress reflection losses. However, the issues of thermal mismatch between the various layer materials of AR coatings makes their AR property unstable, thus limiting their bandwidth and practicality. On the other hand, subwavelength grating (SWG) structures have gained enormous interest recently, mainly in the field of photovoltaics due to several interesting advantages. For example, integrating a SWG onto the top surface of a solar cell device provides an almost a lossless reflecting surface that enhances the solar cell’s efficiency [1]. A SWG often takes a one-and/or two-dimensional periodic form. If the pitch (or period) of a single grating structure is less than the wavelength of the incident light, it behaves like an homogeneous medium with an effective refractive index [1]. Thus, SWG structures give gradual changes in the refractive index assuring an excellent antireflective medium along with a light trapping phenomena in comparison to the planar thin films [2–4]. A nanorod structure acts as a single layer AR coating, while triangular (conical) and parabolic shaped grating structures are more advantageous since they behave like a multilayer broadband AR coating [2].
In this paper, we describe annealing approaches for controlling the size and spacing of silver nanoparticles that act as etch masks for the development of low-reflectivity sub-wavelength structures. Silver nanoparticles formed onto Si or GaAs substrates by thermal annealing enable conical shaped SWG structures to be realized through dry etching. Results show several silver (Ag) thin films of thicknesses 10nm, 8nm and 5nm deposited on GaAs and Si substrates and annealed at different temperatures, leading to the development of randomly distributed silver nanoparticles on the surface of each sample. The diameters and spacing of the Ag nanoparticles are controlled by varying the annealing temperature and film thickness, leading etch masks tailored for different profiles, which can be used in conjunction with etching processes for the realization of SWG structures of various characteristics. FDTD simulation of the SWG structures confirms that much lower anti reflection can be attained in comparison with non-patterned semiconductor substrates.

2. Theoretical Background and Experimental results

The use of SWG structures was inspired by a natural model, moth’s eyes. The surface of a moth’s eye is covered with a nano-structured film that absorbs most of the incident light with minimal reflection. The nano-structured film, which consists of a hexagonal bump pattern, is 200 nm high and acts as an AR coating because the bumps are smaller than the wavelength of visible light. The refractive index between the air and the surface changes gradually, in which case the reflection of the light is also decreased. This model is being applied in solar cells to increase the cell conversion efficiency by allowing large amount of electromagnetic waves to reach the embedded charge carrier zone [4].

However, in order to develop practical SWG structures, several issues must be overcome, including (i) optimising the SWG pattern to maximise the AR property for each application, (ii) the ability to fabricate uniform patterns with appropriate shapes, such as conical, triangular or parabolic and (iii) develop such patterns over large areas cost-effectively.

Two main methods have been reported for the fabrication of SWGs, namely, the lenslike shape transfer process and the Ag nanoparticle process. The lenslike shape transfer method employs laser interference lithography (LIL) in conjunction with thermal reflow, which lead to pattern transfer. This approach requires long photolithography processes and is practical for small-area devices. On the other hand, dry etch processes based on thermally dewetted Ag nanoparticles have been used for the development of large-area SWGs. While this approach is cost effective, it yields SWGs with random shape and spacing, as well as non-optimized antireflection properties. However, if the distribution of the shape and spacing can be controlled, the attained AR properties can still be much better than non-patterned semiconductor surfaces.

2.1. Antireflective coating and SWG structure

The etching of Si or GaAs substrates on which Ag nanoparticles are embedded, results in the formation of SWGs which act as antireflective coatings that enhance the transmission through the substrates. As mentioned earlier, minimum reflection can be obtained through multilayer thin-film coatings [1], however, in addition to their complex fabrication process [1–3], such optical coatings have practical drawbacks, such as adhesion and material mismatching, making the thin-film mechanically unstable and susceptible to thermal fluctuations.
For the rectangular-shaped grating structure shown in Fig. 1, the refractive index changes very sharply from air ($n = 1$) to the grating zone or structure (approximately 2.5 at TM mode) [1]. The reflection loss can be calculated easily using Fresnel’s equation:

$$R = \left( \frac{n_2 - n_1}{n_2 + n_1} \right)^2$$

(1)

where $n_1$ is the refractive index of first medium and $n_2$ is the refractive index of second medium. The total reflection of a SWG structure can be calculated using the following equation:

$$R_{total} = R_1 + R_2$$

(2)

where $R_1$ is the reflection at the interface of air and grating structure and $R_2$ is the reflection at the interface of the grating structure and substrate.

If the SWG structure has a shorter period than the wavelength of the incident light, then it acts as an homogeneous medium with an effective refractive index [3]. According to Fig. 1, the refractive index of a rectangular-shaped SWG structure changes suddenly at the air-SWG interface, however, for the conical shaped SWG structure, the effective refractive index changes gradually, resulting in lower reflection [3]. For a parabolic-shaped SWG structure, the reflection can be as low as 5% over the entire solar spectrum [1].

![Fig. 1. Grating geometry and plot of subwavelength grating (SWG) height versus refractive index (n) in silicon (Si)](image)

### 2.2. SWG fabrication steps

There are several conventional methods for the fabrication of conical SWG structures, such as photolithography, colloidal formation, nanoimprint and nanoparticles. Unfortunately, perfect conical shapes cannot be obtained by any of these methods. The formation of uniformly distributed nanoparticles and the use of dry etching in conjunction with additional isotropic etching processes can produce SWG with almost conical shapes. Fig. 2 illustrates the fabrication steps for creating the SWG structure, which were reported by Song et al. [2].

At first, the nanoparticles can be formed using the annealing process, then CF$_4$ or O$_2$ gas is passed through them using the dry plasma etching process. To shape the formed nanorods in a perfect conical shape, an additional isotropic etching process can be used as reported in [2, 4]. In this paper, the fabricated Ag nano-particles were proposed to be used as a mask to realize the conical shapes in a two-dimensional grid-like distribution to realize the SWG structure.
2.3. Experimental results

Silver (Ag) nanoparticles on GaAs and silicon were fabricated through initial sputtering and subsequent annealing. Annealing was performed in an oven placed in an aerobic environment. After setting the temperature, time and ramp, the oven was allowed to reach the desired temperature and then cool down to ambient temperature.

Ag thin films of thicknesses 10 nm, 8 nm, 5 nm were deposited onto GaAs and Si substrates and annealed at different temperatures, namely 523 K, 573 K, 623 K, 673 K and 723 K. Characterization of the annealed samples was carried out using the SEM method and ImageJ software.

Figure 3 shows the SEM image of Ag nanoparticles on GaAs substrates. The average diameter and average distance between nearest nanoparticles were measured by ImageJ software package. With the recorded data, we simulated the reflection of an SWG structure having a triangular pattern of base size and spacing equal to the average nanoparticle diameter and spacing respectively, using Opti-FDTD software package (developed by Optiwave Inc.) [5]. This software package numerically solves the Maxwell’s equations within a certain medium, the light propagation, scattering, reflection and polarization. Simulation results showing the electric field distribution for the conical shaped SWG structure are shown in Fig. 4. The incident light hits directly on top of the SWG grating structure (or nano-structure). A major portion of incident electromagnetic wave is
absorbed by the grating zone due to the gradual change of refractive index, while the rest is reflected or transmitted.

Fig. 4. Schematic diagram of conical shaped subwavelength grating (SWG) structure and the steps for simulating the propagation of the electromagnetic waves across the simulated structure

Fig. 5 shows the average spacing between the silver nanoparticles versus the annealing temperature for a 10 nm thick Ag thin film deposited onto Silicon and GaAs substrates. It is obvious that for the silicon substrate, the average spacing of 200 nm is maintained over the temperature range of 520-575 K, whereas for a GaAs films the spacing increases with increasing temperature (this is, however, useful for some applications required some degrees of spacing control).
Fig. 5. Average spacing $S(\mu m)$ between the Ag nanoparticles versus annealing temperature for a 10 nm Ag thin film deposited onto Si and GaAs substrates.

Fig. 6 shows the reflection spectra for Ag films of different thicknesses deposited onto Si and GaAs substrates, and annealed at different temperatures. It is seen from Fig. 6 that a 10 nm thick Ag film on Si annealed at 523 K yielded a maximum reflection as low as 12%, while the 8 nm thick Ag film, annealed at 573 K, resulted in maximum reflection of 13%. The 5 nm thick Ag film which was annealed at 623 K produced maximum reflection below 7% over a wide range of wavelengths. Conversely, the Ag film on GaAs annealed at 523 K showed reflection below 10% over a wide range of wavelengths. The 8 nm Ag film on GaAs annealed at 673 K exhibited lower reflection in comparison with other annealing temperatures, and the reflection of the 5 nm Ag film on GaAs annealed at 723 K was as low as 15%.

3. Conclusions

Ag thin films with different thicknesses have been deposited on semiconductor substrates and annealed at different temperatures to fabricate Ag nano-particles that can be used to cost-effectively develop SWGs that perform as AR coatings for semiconductor devices. We have found that the desired diameter and spacing between nanoparticles can be achieved by controlling the annealing temperature and Ag film thickness that can be ultimately used to fabricate SWG structures having patterns of arbitrary sizes and spacing, which control the reflective properties.

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References

Fig. 6. Reflection spectra for various SWG structures developed using 10 nm, 8 nm and 5 nm thick Ag films on Si and GaAs substrates, annealed at different temperatures.

