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Broadband near-infrared absorption enhancement in Si substrate via random distributed Ag nanoparticles

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Abstract A broadband near-infrared (NIR) absorption from 1200 to 2500 nm in Si substrate is investigated by Ag film deposition and subsequent thermal annealing. Under thermal annealing, Ag films can crack and shrink into Ag nanoparticles (NPs). Annealing temperature greatly affects the size, distribution status and morphology of Ag NPs, resulting in different NIR absorption. The influence of the size and distribution of Ag NPs on NIR absorption originated from localized surface plasmon resonance (LSPR) is theoretically simulated by a finite difference time domain method. The band width of LSPR belongs to different type Ag NPs are discussed.

1 Introduction

It is known that traditional silicon (Si) optoelectronic devices are far better than non-Si devices because they have many great advantages such as low cost, high performance and mature technology. However, due to their large energy-band gap (1.12 eV), the response range of Si devices is mainly concentrated in the visible region (<1.1 μm), which severely limits their applications in the infrared range. In order to overcome this limitation, many approaches have been proposed to extend its infrared absorption, including black silicon technology [1–6], nano-antennas [7–10] and grating structures [10, 11]. Although these researches obtained some achievements, they had a common drawback that the preparation process is complicated and costly.

In recent years, the investigations on the surface metallic nanoparticles (MNPs) have attracted considerable interest because there exists localized surface plasmon (LSP) induced by MNPs structure at metal-dielectric interface [12]. People's enthusiasm on the MNPs structure can mainly be ascribed to its ability that the incident light will be absorbed by microstructure significantly when its frequency matches LSP frequency, which is named localized surface plasmon resonance (LSPR) [12]. This special property brings possibilities to realize widely new function of Si-based material. In some reports, the MNPs structures have been utilized to enhance the emission of light-emitting diodes (LEDs) [13, 14]. Moreover, other research groups use MNPs to realize broadband antireflection on the silicon surface [15]. Certainly, the most important significance is to enhance Si-based material absorption in the interest waveband by the MNPs structures [12, 16–18]. However, major investigations of absorption enhancement through MNPs structure are concentrated on visible range rather than near-infrared (NIR) range [16, 17]. Meanwhile, it generally exhibits a narrow band absorption enhancement [16] which is impractical for applications requiring broadband absorption, for instance, photovoltaic and photodetectors. Accordingly, a broadband NIR absorption from 1200 to 2500 nm in Si substrate is investigated by Ag film deposition and subsequent thermal annealing in this study. Randomly distributed Ag nanoparticles (NPs) with different sizes generated by thermal annealing induce the excitation of multiple LSPRs at Ag-Si interface, resulting in a broadband NIR absorption enhancement. The influence

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of the size and distribution of Ag NPs on the absorptance (A) is theoretically analyzed in detail.

2 Experimental details

The preparation process of Ag NPs is shown in Fig. 1. After chemical cleaning of surface native oxide in hydrogen fluoride and acetone solutions, 20 nm-thick Ag thin films are coated on a 450 μm thick single-side polished boron-doped (10 Ω cm) Si wafer by thermal evaporation at a rate of 0.5 Å/s. Then the sample is thermally annealed in a furnace with N_2 ambient for 30 min, leading to that Ag films crack and shrink into Ag NPs. The annealing temperature is set to 450, 550 and 650 °C, respectively. The surface morphology of Ag NPs is characterized by means of a scanning electron microscope (SEM, JSM-6510 of JEOL) and an atomic force microscope (AFM, EDG of Bruker). The integrated reflectance (R) and transmittance (T) spectra between 1200 and 2500 nm are measured in a spectrometer (PerkinElmer Lambda-1050) equipped with a 160 mm integrating sphere, from which the integrated A spectra was extracted through $A = 1-R-T$.

3 Results and discussions

Figure 2 shows the top-view SEM images of Si covered with Ag films annealed at different temperatures. Particle size distribution histogram of each sample is plotted under the corresponding SEM image. Obviously, both the random size and shape of Ag NPs have a great relationship with annealing temperature. The higher the annealing temperature, the more fully the Ag film would crack, and the larger the distance between the particles would be. While as the temperature rises, the total number of particles reduces, but the size of each Ag NP is growing. Figure 3 shows the AFM images of Si covered with Ag films annealed at different temperatures. The evolution of Ag NPs from AFM images is agreement well with that from SEM images. Compared to the SEM image, however, AFM image can quantitatively reflect three-dimensional morphology of Ag NPs, from which the evolution of Ag NP volume is more intuitive with annealing temperature increasing.

Figure 4 shows the near-infrared absorption spectra of Si covered with Ag films annealed at different temperatures, where Si covered without Ag films is also given. Before thermal annealing, Si covered with Ag film exhibits an increasing absorption compared with pure Si wafer, which is induced by the intrinsic absorption of Ag films. Meanwhile, there exists a manifest further increase after thermal annealing and, in particular, the average A is improved to approximately 30 % in the broadband range from 1200 to 2500 nm under 550 °C annealing. By comparison of it, although the absorption under 650 °C annealing has a little decrease with a reasonable cause that large particle size (see Fig. 2) results in an increasing surface scattering, the experimental results indicate that Ag NPs have a great effect on the absorption enhancement of NIR light in a broadband range.

It is known that MNPs can enhance light absorption through the LSPRs. Generally, LSPRs induced by single-type MNPs lead to a narrowband absorption peak [16] while a broadband absorption enhancement from 1200 to

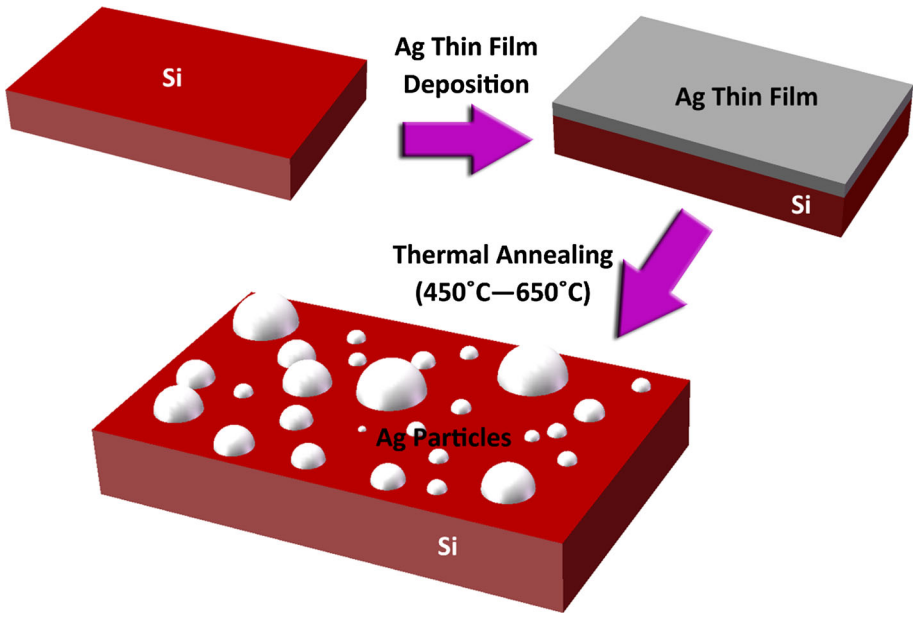

Fig. 1 Preparation process diagram of Ag nanoparticles on Si substrate

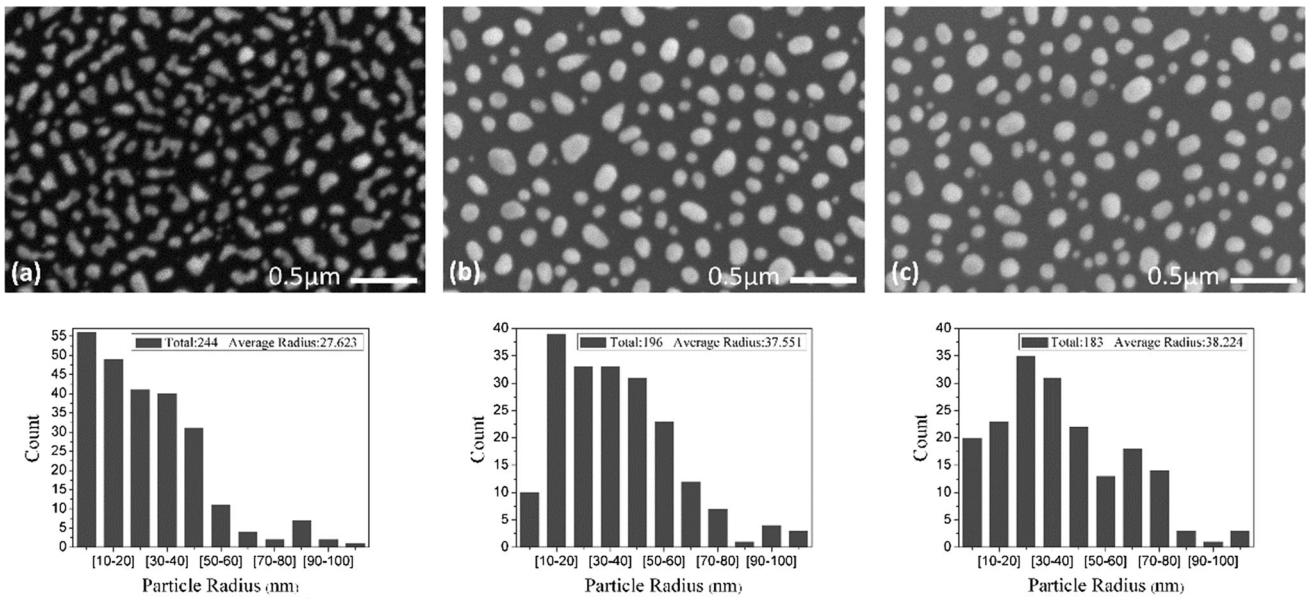

Fig. 2 Top-view SEM images of Si covered with Ag films annealed at **a** 450 °C, **b** 550 °C and **c** 650 °C. Particle size distribution histogram of each sample is plotted under the corresponding SEM image

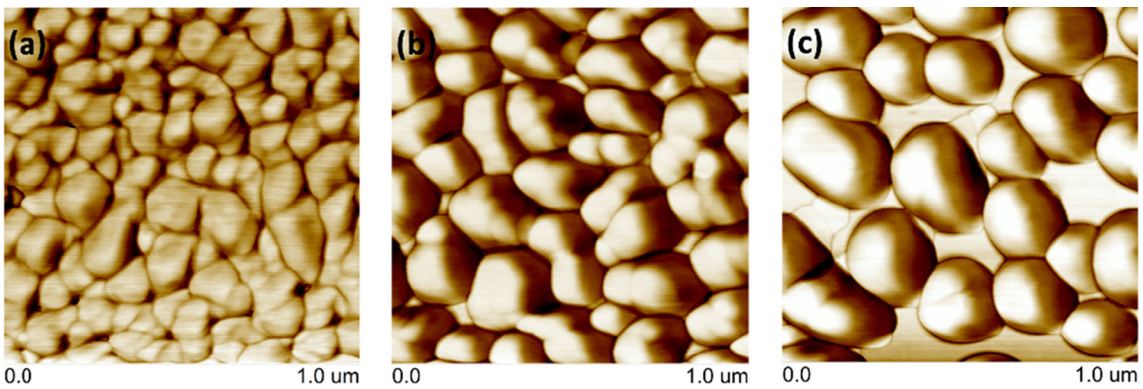

Fig. 3 AFM images of Si covered with Ag films annealed at **a** 450 °C, **b** 550 °C and **c** 650 °C

2500 nm are observed in this study. This should be strongly relative to the size and distribution of Ag NPs on Si surface [12, 16]. In order to clarify that, three sets of finite difference time domain (FDTD) simulations were carried out to calculate the absorption of Ag NPs structure covering on Si substrate. A linearly polarized light is used as the normal incidence source, and we would not discuss it in any further detail because we find that the simulated absorption results under any polarized direction are almost identical. As for the boundary condition, the periodic condition is set up in simulations due to the macroscopic homogeneity of MNPs structure.

In the first set of simulations, we calculated the absorption spectra of identical Ag NPs periodically distributed on Si substrate, as shown in Fig. 5, in which the particle size was changed from 40 to 70 nm to observe the effect of particle size on the absorption peak position and the periodicity that three times longer than particle size was chosen. We determined the range of particle size and periodicity on the basis of top-view SEM images and statistics histogram of Fig. 2. The absorption spectra show a narrowband resonant absorption enhancement in the NIR range excited through LSPRs. Moreover, it is confirmed that the resonant wavelength exhibits a red-shift behavior as the particle radius increases. This result illustrates that particle size would actually affect the absorption peak position of the Ag NPs structure.

In the second set of simulations, we compared the absorption spectra of identical Ag NPs with different distribution status on Si substrate, as shown in Fig. 6. It was changed from periodical to random to indicate the effect of particle distribution on the width of absorption band. In this

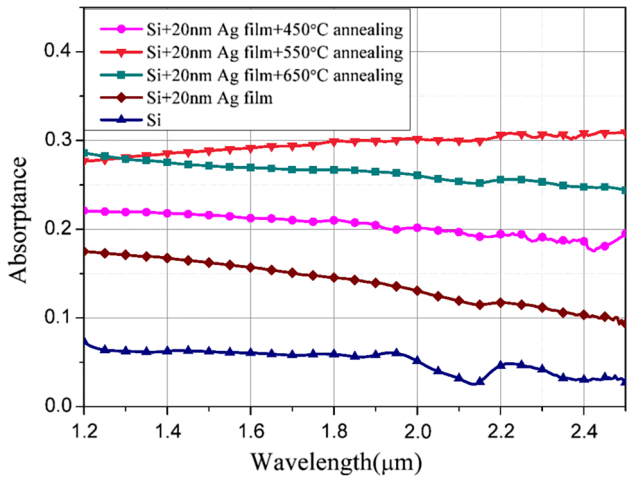

Fig. 4 Near-infrared absorption spectra of Si covered without and with Ag films annealed at different temperatures

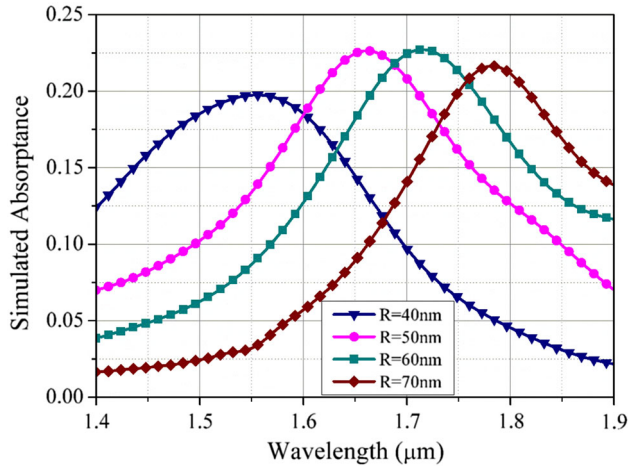

Fig. 5 Simulated absorption spectra of identical Ag nanoparticles periodically distributed on Si substrate. The periodicity that three times longer than particle size was chosen and the particle radius was changed from 40 to 70 nm

set of simulations, the radius of Ag particle is 50 nm. Obviously, Si substrate with periodically distributed Ag NPs has a narrowband absorption enhancement while it presents a very broad absorption band when Ag NPs change to random distribution, which indicates that random distribution can broaden the absorption range. For randomly distributed Ag NPs, it is possible that some particles are close to each other and their distance is less than a radius of particles, which means the interaction between particles cannot be ignored [12]. According to the expression of resonance frequency [12], the interaction could reduce the resonance frequency and result in the additional red-shift and broadband of resonance frequency, which is in agreement well with our simulation results above.

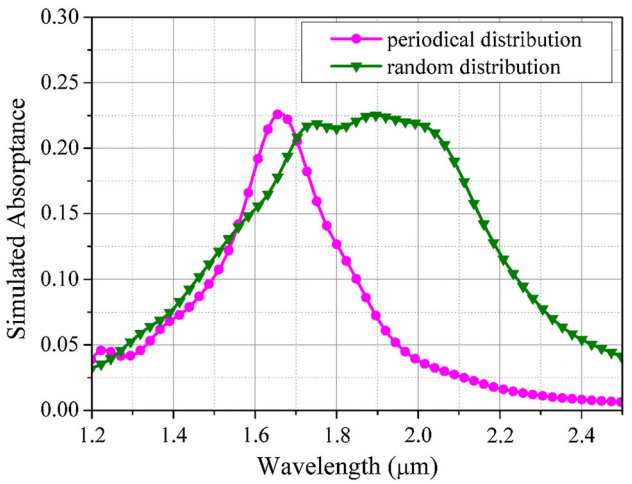

Fig. 6 Simulated absorption spectra of identical Ag nanoparticles with different distribution on Si substrate. Ag particle radius is set to 50 nm

As shown in Fig. 7, in the third set of simulations, we further calculated the absorption spectra of Ag NPs with random distribution status and various sizes, altering from 10 to 100 nm. From Fig. 2, it can be confirmed that Ag particles with the size of several ten nanometers are dominantly distributed on the substrate surface; therefore this range of particle size that we set up in this set of simulations could include almost all values of particle size in experiments. By comparison of Figs. 6 and 7, clearly the size change of randomly distributed Ag NPs further broadens the absorption spectra. According to the results of Fig. 5, this phenomenon is mainly because multiple LSPRs' bands are generated due to a variety of particle sizes. In addition, its absorption is much higher than that of 20 nm-thick Ag film covering on Si substrate without

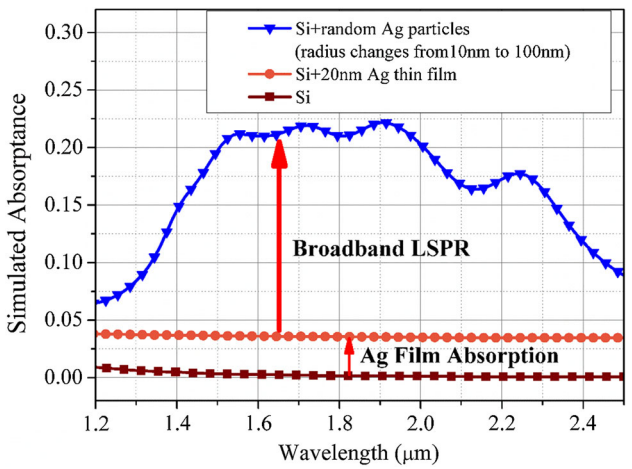

Fig. 7 Simulated absorption spectra of randomly distributed Ag particles with different radius changed from 10 to 100 nm. As a comparison, Si with and without 20 nm-thick Ag films are also given

thermal annealing, which is largely owing to LSPRs excited by NPs. In view of the three sets of simulations mentioned above, it is concluded that the random distribution status and the various sizes of multiple-types Ag NPs contribute a broadband LSPRs, causing the broadband NIR absorption enhancement in Fig. 4.

4 Conclusion

We successfully demonstrated the NIR absorption enhancement in Si substrate by Ag film deposition and subsequent thermal annealing. It was found that Ag films cracked and shrank into Ag NPs after thermal annealing. The particle size, distribution status and morphology showed a strong dependence on annealing temperature. Under 550 °C annealing, the average A was improved to approximately 30 % in the broadband range from 1200 to 2500 nm. Theoretical simulation indicated that the random distribution and the various sizes of multiple-types Ag NPs contributed to broadband LSPRs, resulting in the NIR absorption enhancement in a wide waveband.

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