Development of a Near-infrared Reflective Film Using Disk-shaped Silver Nanoparticles

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Abstract

FUJIFILM Corporation has developed a novel near-infrared reflective film using disk-shaped silver nanoparticles. We estimated the best shape and arrangement of the silver nanodisks to reflect near-infrared rays by simulation. In order to form an optimum structure, we applied the technology which has been used to form silver halide tabular grains in photographic film. Moreover, we have developed the coating technology to make a uniform layer of silver nanodisks that reflect near-infrared rays effectively.

1. Introduction

With the recent increase in demand for energy savings, heat barrier films have been attracting more attention. Affixed to windows, they block infrared light and thereby decrease cooling load. We developed a new, near-infrared reflective material, using disk-shaped silver nanoparticles, or silver nanodisks[1) to 4)], that can be applied to those films (Fig. 1).

Among such films, the most desired on the market lately are the ones that can block as much infrared light as possible while having a high visible-light transmittance. Fig. 2 shows the solar energy spectrum. Nearly half of solar energy is from infrared light. In particular, energy from the near-infrared region (wavelength of 800 nm to 1,100 nm) is considerable. Therefore, materials that can block near-infrared light are highly demanded. Of the infrared light-blocking materials, reflection types are preferable because absorption types are not very effective, allowing some heat to radiate into rooms.

There are already some heat barrier film products made of near-infrared reflective materials on the market. However, they have some issues in conforming to curved surfaces and in radio-wave transparency. Therefore, we developed a new, near-infrared reflective material to solve those two problems together.

This paper describes the ideal near-infrared reflective structure determined via simulation, a novel technology developed to achieve that structure and the performance of heat barrier films using the material realized based on them.

2. Design of the near-infrared reflective structure using a metamaterial with a silver nanodisk arrangement

To realize a structure that achieves the desired properties, we turned our attention to metamaterials based on the principle of localized plasmon resonance (LPR). LPR is collective motion of free electrons inside metals in resonance with the vibration of the electric field of light. Light is absorbed and scattered intensely near the resonant frequency.

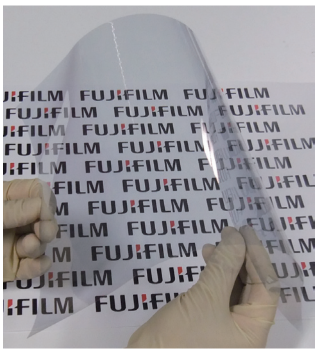

Fig. 1 Near-infrared reflective film using silver nanodisks.

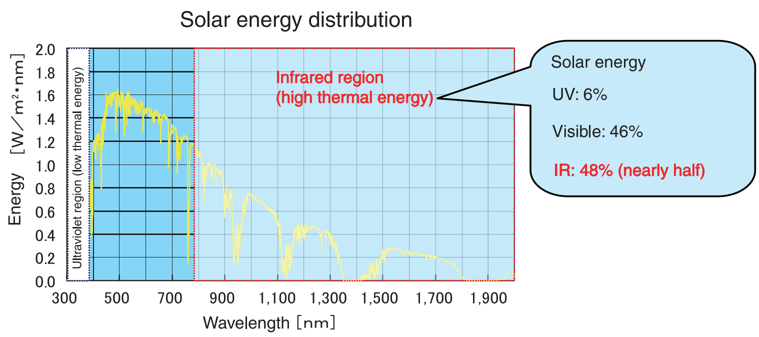

Fig. 2 Solar energy distribution.

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It is possible to control the frequency of LPR and the tendencies of the scattered light by the size and shape of the metallic nanostructure and its arrangement. Therefore, LPR technology has played a central role in the field of metamaterials to realize unique light properties artificially with nanostructures. LPR occurs most readily in low electrical-resistance precious metals. Among those metals, silver is known to cause the strongest LPR. Based on the above fact, we used a silver nanostructure with the aim of realizing a metamaterial that reflects only near-infrared light while achieving transparency to visible light and radio waves.

To accurately predict properties such as light scattering decided by the shape and arrangement of nanoparticles, we employed a computational electromagnetics technique, the finite-difference time-domain (FDTD) method. Via simulation, we investigated the ideal structure and discovered that, if silver nanodisks can be arranged like a stone pavement as shown in Fig. 3, the intended properties could be realized. The following are the details of that structure.

The shape of the silver nanodisks is an important parameter to control resonance wavelengths. Round silver particles are resonant with visible light. However, if they are shaped into flat disks, by adjusting the aspect ratio (division of the equivalent circle diameter by thickness), silver nanoparticles can be resonant with a wider range of wavelengths from visible light to infrared light[5]. Fig. 4 shows examples of the extinction cross section calculated with different aspect ratios of silver nanodisks. The results indicate that nanodisks with an aspect ratio of about 10 or larger can be resonant in the infrared region.

The key parameter to control reflectance is the distribution of silver nanodisks. Fig. 5 shows the comparative results of simulations for the optical properties of the single-particle system and the silver monolayer dispersion system. In the

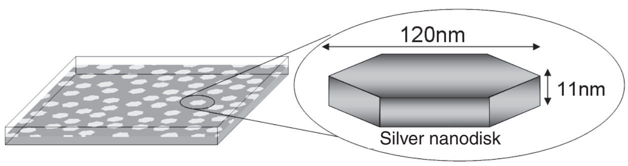

Fig. 3 Best formation and arrangement of silver nanodisks estimated by simulation.

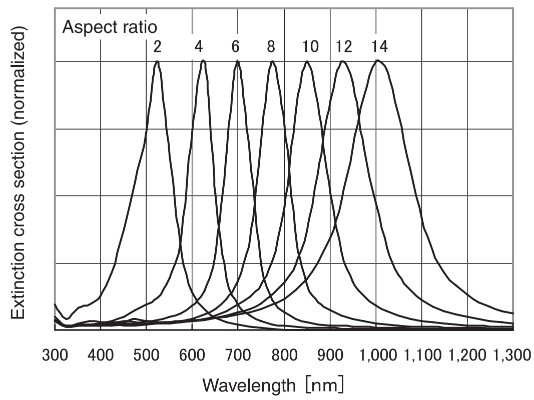

Fig. 4 Resonance wavelength variation according to the aspect ratio of silver nanodisks.

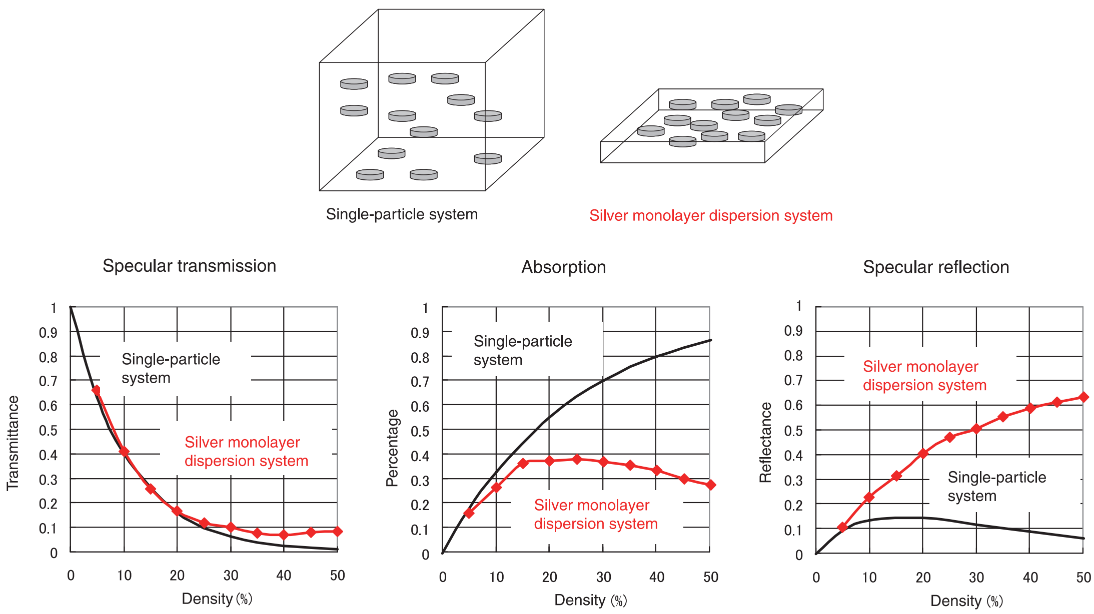

Fig. 5 Spectra of isolated dispersion and monolayer dispersion.

former, silver nanodisks are distributed widely throughout the layer thickness while, in the latter, they are aligned on the same plane. The properties shown in the figure were gained under an infrared radiation of 900 nm set as the central value for plasmon resonance. The results reveal that, in the resonant state of the former, energy is lost mainly by absorption after being scattered but, in the resonant state of the latter, reflection is dominant over energy loss via scattering. That could occur because the dense arrangement of silver nanodisks on the same plane allows plasmon resonance to grow into an electromagnetic field vibration over a larger region across multiple nanoparticles, which facilitates the release of the electromagnetic waves of light to the outside.

The results of the above simulation conducted based on nanophotonic knowledge brought us to the conclusion that, to achieve high visible-light transparency and high near-infrared reflection together, a structure with the following characteristics is optimal.

(1) A film in which silver nanodisks are aligned on the same plane with the proper density.
(2) The thickness of nanodisks being 11 nm with an equivalent circle diameter of 120 nm.
(3) The area packing ratio of the silver being 35%.

3. Manufacture of near-infrared reflective materials

Initially, it was considered to be highly difficult to manufacture the optimum structure derived from the simulation, in particular, on a mass-production scale. However, by applying photographic film technology, we succeeded in the creation of the desired film.

There already exists a photographic film technology to form disk-shaped, silver halide particles and apply them orientated in a plane. We considered a way to create a structural film by utilizing such technology to shape silver nanodisks and arrange them with an appropriate density orientated in a plane.

It was possible to form silver nanodisks in a similar way to silver halide particles, because silver halides and silver belong to the same crystallization system. Fig. 6 shows the manufacturing flow.

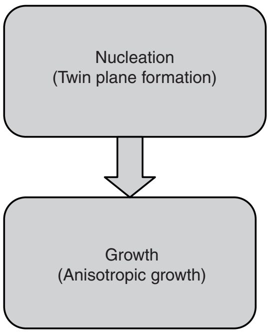

Fig. 6 Flow of silver nanodisk formation.

After establishing the environment for the nucleation process, we first formed twin plane of silver. Because of their natural tendency of growing anisotropically, they could easily grow into disk-shaped particles. In the growing process, too, while growing them under conditions that enhance that tendency, we then manufactured silver nanodisks. By adjusting the growing conditions, we finally succeeded in the creation of the intended silver nanodisks with a thickness of 11 nm and an equivalent circle diameter of 120 nm.

The silver nanodisks thus created cannot form a high-reflectance film by simply applying them, as the nanodisks will be facing in different directions within the coated layer as shown in Fig. 7. It is likely that this occurs because the nanodisks were distributed widely throughout the layer thickness as seen in single-particle system. By applying them under specified conditions, silver nanodisks was able to be arranged like a stone pavement without overlapping one another (Fig. 8).

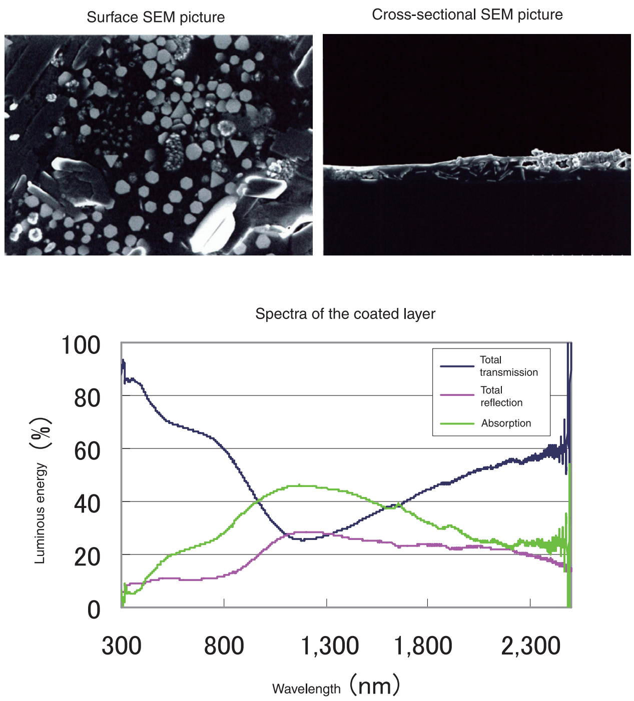

Fig. 7 SEM pictures and spectrum of coating film (before using coating technology).

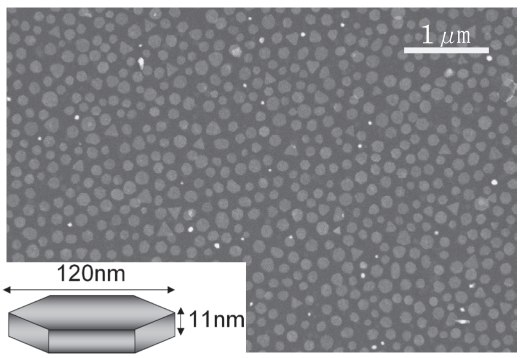

Fig. 8 SEM picture of coating film.

Fig. 9 shows the spectral performance of this coated film. The results of the optical simulation and actual measurement are consistent and have realized high visible-light transparency and high near-infrared reflectance together.

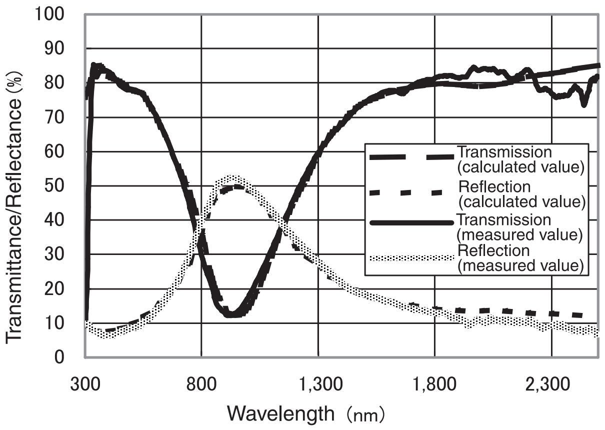

Fig. 9 Experimental and calculated spectra.

4. Characteristics of the near-infrared reflective material

The following are the characteristics of the near-infrared reflective material that we have developed.

(1) Infrared reflection: At the peak of its blocking performance, a large amount of reflection can be detected together with absorption.

(2) Radio-wave transparency: Less than 0.2 dB using the KEC measurement method

(3) No shifts by angle-of-view dependence occur at the peak of its blocking performance.

(4) Good conformation to curved surfaces

5. Application to construction-use heat barrier films

Having applied the heat barrier film made of the newly developed near-infrared reflective material to a window, we conducted an experiment to verify its performance. As a result, the temperature around the window became lower by up to 6.5°C. We then prepared two rooms, with and without the heat barrier film applied, and checked the power consumed by their air conditioners. In the room with the film, the power consumption was reduced by 15% at its peak.

Films made of this near-infrared reflective material are already available on the market for construction-use film manufacturers. They are used in heat barrier films for buildings.

6. Conclusion

Via optical simulation, we derived a film structure that is both transparent and capable of obtaining selective reflection of the near-infrared region and succeeded in the creation of a silver nanodisk-arranged film based on that structure in an actual coating. The film exhibited the property of reflecting near-infrared light as predicted by the simulation.

References

1) FUJIFILM Corporation. Polyfile. **49** (581), 32-33 (2012).

2) Hakuta, S.; Tani, T.; Kiyoto, N.; Kamada, K.; Naya, M. Wavelength-selective Shielding Film with a Silver Nanodisk Monolayer Dispersion Structure. Proceedings of the 59th Meeting of The Japan Society of Applied Physics and Related Societies. 18a-B11-2 (2012).

3) Kiyoto, N.; Hakuta, S.; Kamada, K. Development of Near-infrared Reflective Material Using Disk-shaped Silver Particles. The Society of Photography and Imaging of Japan. **75** (2), 158 (2012).

4) FUJIFILM Corporation. Matsunami, Y.; Kiyoto, N.; Hakuta, S.; Tani, T.; Naya, M.; Kamada, K. *Tokukai* (Japanese Published Unexamined Patent Application) No. 2011-118347. 2011-6-16.

5) Jin, R. et al. Nature, **425**, 487 (2003).