

Enhancement of the Photoluminescence of Porous Silicon by Sputter Deposition of Semitransparent Metal Films

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Optoelectronic devices based on porous silicon (PS) undergo substantial degradation in luminescence with aging due to atmospheric oxidation. The passivation of PS has been reported with a transparent conducting material or a semi-transparent metal. In this paper, we report enhancement of the photoluminescence (PL) of PS by the passivation of PS with ultrathin metal films such as silver (Ag), aluminum (Al), and gold (Au). It has been found that Ag and Au are respectively most and least effective in enhancing the PL of PS among those three different metals. The highest PL enhancing effect of Ag is mostly attributed to the high electrical conductivity of Ag, whereas the lowest PL enhancing effect of Au is due to the lowest optical transmittance of Au. The details of the PL enhancing effect of metal passivation are discussed with the aid of FTIR analysis results.

Keywords: porous materials, anodization, sputtering, optical properties, SEM

1. INTRODUCTION

For the past two decades since photoluminescence (PL) and electroluminescence (EL) were discovered in porous silicon (PS), a wide range of research has been performed to realize PS-base optoelectronic devices such as light emitting diodes (LED) [1-3], waveguides [4], optical filters [1,2], photovoltaic diodes [5-7] and various kinds of sensors [8]. Nevertheless, optoelectronic devices based on PS have not been commercialized yet, although PS is a promising light emitting material showing significant luminescence over a wide range of spectra. The luminescence efficiency of PS is still not high enough for high performance optoelectronic devices owing to the very low electrical conductivity of PS and degradation of luminescence. It is important that light emitting be stable. However, the entire surface of PS is covered by hydrogen species such as SiH_x that are unstable when exposed to air. As ambient oxidation proceeds, oxygen is incorporated in SiH backbones, and a silicon film grows, accompanied by the creation of silicon dangling bonds at the Si/SiO₂ interface. The silicon dangling bonds, serving as nonradiative centers, decrease the PL intensity [9].

Many surface treatment techniques have been studied to obtain stable PL. One of these techniques is the passivation

of PS using thermal or anodic oxidation. However, oxidation of PS can easily lead to the coalescence of a porous layer due to the thermal instabilities of the material. Organic modification and high pressure water vapor annealing are also known to be effective for PL stabilization [10,11], but their PL enhancement is not sufficient to realize optoelectronic devices. On the other hand, passivation of the PS layer with a thin transparent conducting oxide or an ultrathin semi-transparent metal layer is a promising technique in enhancing the PL and EL intensities of PS. These materials include indium tin oxide (ITO) [12-14], Al-doped ZnO (AZO) [15], Ga-doped ZnO (GZO) [16], Cu [17], Ag [18,19], and Au [20,21]. These passivation films can be deposited by using various techniques including electroplating [18], spray pyrolysis [22], sputtering [16], and electron beam evaporation [8]. Among these deposition techniques, sputtering may be the simplest one which is applicable to any type of material, including elements or compounds, and offers uniform films [23].

In this paper, we compare the PL properties of PS passivated with ultrathin Al, Au, and Ag thin films deposited by RF-sputtering. The PL property of PS passivated with Au or Ag has been reported before, but there has been no report on the passivation of PS with ultrathin Al films so far; this is perhaps because Al cannot be deposited by electroplating. Furthermore, there has, thus far, been no report comparing their PL properties under the same condition. We also discuss differences among these three passivation materials in

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the passivation effect on the PL property of PS using the FTIR analysis technique. Our results show that the PL intensity of PS can be enhanced by simply depositing an ultra thin metal film on the PS by sputtering.

2. EXPERIMENTAL DETAILS

Electrochemical anodization was conducted to produce PS layers on polished p-type Si(100) wafers with a resistivity of $10 \Omega\text{cm}$ to $12 \Omega\text{cm}$. Prior to anodization an Al contact was formed at the backside of Si wafers by sputtering and was then annealed at 450°C for 30 min in vacuum to make it ohmic. Anodization was carried out in a 1:1 solution of 46 % HF and 95 % ethanol using Pt as the counter electrode at a current density of 30 mA/cm^2 in the dark for 40 min. The porosity of the PS layers determined by weight measurements [24] was about 65 %. After anodization, the PS layers were dried to reduce the capillary stress by using pentane, which has very low surface tension and no chemical reactivity with the PS layer. The samples were then rinsed with 98 % methanol and then with deionized water. Finally, the samples were dried at about 50°C on a hot plate rather than in a N_2 nozzle in order to avoid cracking and peeling of the PS layer.

Three different kinds of ultrathin semi-transparent metal films including Al, Au, and Ag were deposited separately by RF magnetron sputtering at room temperature in the PS layer formed on pieces of a Si wafer, the area of which was about 23 mm^2 . The RF power, the chamber pressure, and the Ar gas flow rate in the sputtering process were 300 W, 0.05 Torr, and 30 sccm, respectively. The sputtering time was varied from 5 s to 20 s with an increment of 5 s to obtain various film thicknesses. Besides these metal coated PS samples, another set of PS samples was coated with these metals and then annealed. Annealing treatment was performed at 700°C for 1 h in a vacuum annealing furnace. The base vacuum level was 10^{-3} Torr.

For these two sets of samples – PS layers passivated with metals and those passivated with metals and then annealed by PL spectroscopy analyses were performed at room temperature with a 325 nm line from a He-Cd laser (Kimon, 1K, Japan). The microstructures of the samples were investigated by using scanning electron microscopy (SEM: Hitachi S4200). The thicknesses of the metal films deposited on the PS layers were measured by using the metal film-deposited dummy Si wafers. Chemical bond structures at the metal – PS interfaces were investigated using a Nicolet 560 Fourier transform infrared (FTIR) spectrometer.

3. RESULTS AND DISCUSSION

Figures 1(a), (b), and (c) show the PL spectra of PS layers passivated with ultrathin Au, Ag, and Al films, respectively.

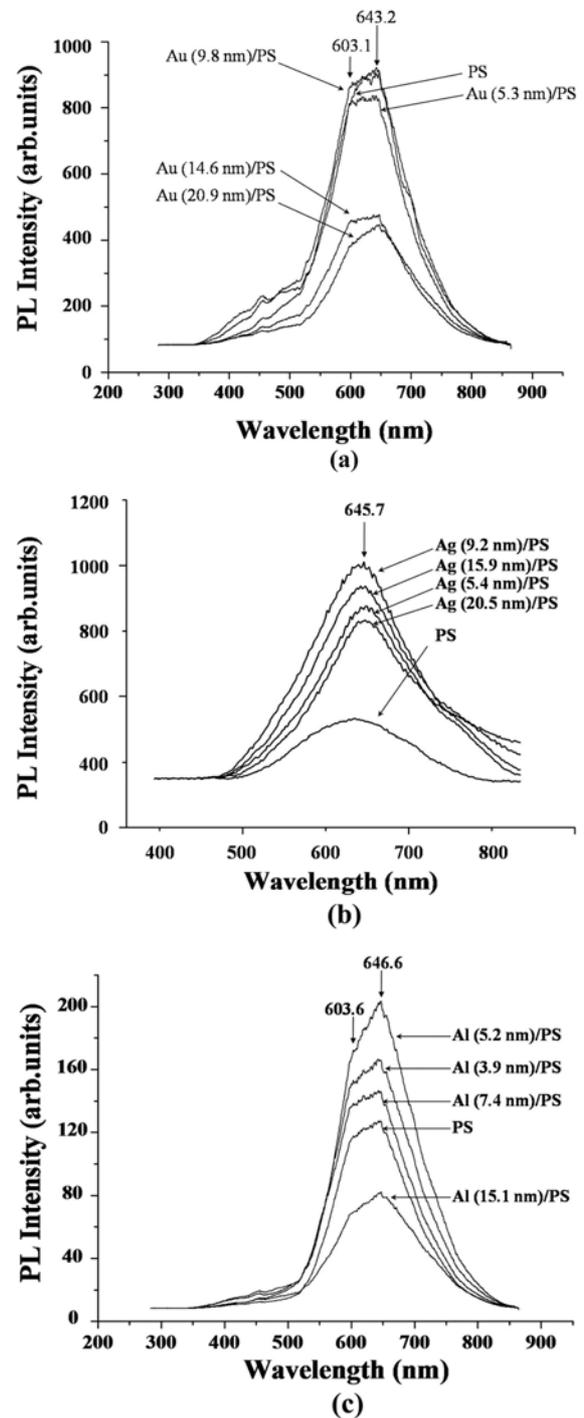


Fig. 1. The PL spectra of (a) Au/PS, (b) Ag/PS, and Al/PS samples with different Au, Ag, and Al film thicknesses, respectively.

All the three PL spectra exhibited a similar broad emission peak centered at 660 nm. This visible emission of PS is known as an S-band. Various models including the quantum confinement model, hydrogenated amorphous silicon model, surface hydrides model, defect model, siloxene model, and surface states model have been proposed to explain the S-

emission band [25]. The quantum confinement model is the most widely accepted among these models although there are still controversies. Each figure contains the PL spectra for five different metal film thicknesses. All those three figures show the same tendency in which the PL intensity increases first and then decreases as the metal layer thickness increases. In other words, the optimum metal thickness exists for each metal. It can be seen in Fig. 1(a) that the highest enhancement in the PL of PS is achieved by the passivation of PS with an Au film with a thickness of 9.8 nm. The PL intensity of PS is increased by $\sim 9.8\%$ compared to that of the uncoated PS by coating the PS layer with a 9.8 nm Au film. In a similar manner, the highest PL enhancement of 83% is obtained by the deposition of a 9.2 nm Ag film (Fig. 1(b)). On the other hand, the highest PL enhancement of PS obtained by 5.2 nm Al deposition is 67% (Fig. 1(c)). Figure 1 also indicates that the minimum full width at half maximum (FWHM) of the PL peak is obtained for the 9.8 nm Au, 9.2 nm Ag and 5.2 nm Al films, respectively, suggesting that the FWHM of the PL peak can be explained by the same physical origin as the PL intensity, which will be discussed in detail later. The results summarized in Table 1 indicate that Ag is most effective in enhancing the PL of PS among Au, Ag, and Al.

We must use a passivation metal film with the optimum thickness to maximize the PL enhancing effect. The optimum thickness of the passivation metal film exists via the trade-off of two opposing factors as follows. First, PL is a phenomenon in which light is emitted when electrons and holes recombine with each other in a solid. The total number of carriers or the carrier concentration in the metal-coated PS will increase as the thickness of the metal layer increases. Consequently, the probability of the recombination of electrons and holes will increase, and, thus, the PL intensity of the PS passivated with a metal film increases as the thickness of the metal layer increases. Second, as the thickness of the metal film increases, the final PL intensity of the metal-coated PS decreases because the light emitted from the PS must pass through the metal layer.

Table 1 show that Ag passivation is most effective in enhancing the PL emission intensity in spite of the relatively low optical transmittance of the 9.2 nm Ag film, while Au passivation is least effective in enhancing the PL of PS among the three different kinds of metals. The high PL enhancing effect of Ag passivation must be attributed to the high elec-

Table 1. The maximum PL intensities of PS deposited with different metal films

Sample	Max PL intensity			Wavelength (nm)	Metal film thickness (nm)
	I_{max}	I_o	I_{max}/I_o (%)		
Au/PS	910	895	101.7	643.2	9.8
Ag/PS	1000	546	183.2	645.7	9.2
Al/PS	210	126	167.0	646.6	5.2

Table 2. The transmittance of ultrathin metal films measured at the wavelength for the maximum PL

Sample	Transmittance (%)	Wavelength for max. PL (nm)
Au (9.8 nm)/glass	56	643.2
Ag (9.2 nm)/glass	63	645.7
Al (5.2 nm)/glass	90	646.6
glass	92	

Table 3. The electrical conductivities of Au, Ag, and Al

Metal	Electrical conductivity (S/m)
Ag	63.01×10^6
Au	45.2×10^6
Al	37.8×10^6

trical conductivity or carrier concentration of Ag since Ag is the highest conducting material among all elements, as shown in Table 3. It is well known that a metal with a larger number of valence electrons has higher conductivity because all the valence electrons act as conduction electrons in metals. In reality, the assumption that all valence electrons become conduction electron while the others remain bound to the ions is not true. The electrical conductivities of metals are, however, intimately related to the electrons only in the s state of the valence band. In comparison with Au and Al atoms, an Ag atom has higher electron density in the s state of the valence band than the other two although the number of the electrons in the valence band is smaller in an Ag atom than those in Au and Al atoms. Ag also has higher carrier mobility than Au and Ag [26].

Table 1 indicates that the PL enhancing effect of Au passivation is inferior to that of Al passivation despite the fact that the electrical conductivity of Au (45.2×10^6 S/m) is higher than that of Al (37.8×10^6 S/m) [27]. The inferiority of Au passivation may be caused by the low optical transmittance of Au. The ultrathin metal film samples used for measuring transmittance were prepared by depositing the metal films on a transparent silica glass substrate whose transmittance was about 92%. The optical transmittance spectra of Au (9.8 nm)/glass, Ag (9.2 nm)/glass, and Al (5.2 nm)/glass samples are shown in Fig. 2. The transmittances of Au (9.8 nm), Ag (9.2 nm), and Al (5.2 nm) at wavelengths of 643.2, 645.7, and 646.6 nm for the maximum PL read from Fig. 2 are 56, 63, and 90%, respectively, as summarized in Table 2. As shown in Table 2, the transmittance (56%) of the 9.8 nm Au film is by far lower than that (90%) of the 5.2 nm Al film. An intrinsic property influencing the transmittance of a metal is high oxidation- or corrosion-resistance. The transmittance of a metal is generally decreased by oxidation. The lower transmittance of Au than Ag and Al given in Table 2 may be because the Au thin film has not nearly oxidized while the surface region of the Ag and AuAl thin films had been already oxidized (by native oxidation). Hence, the lower

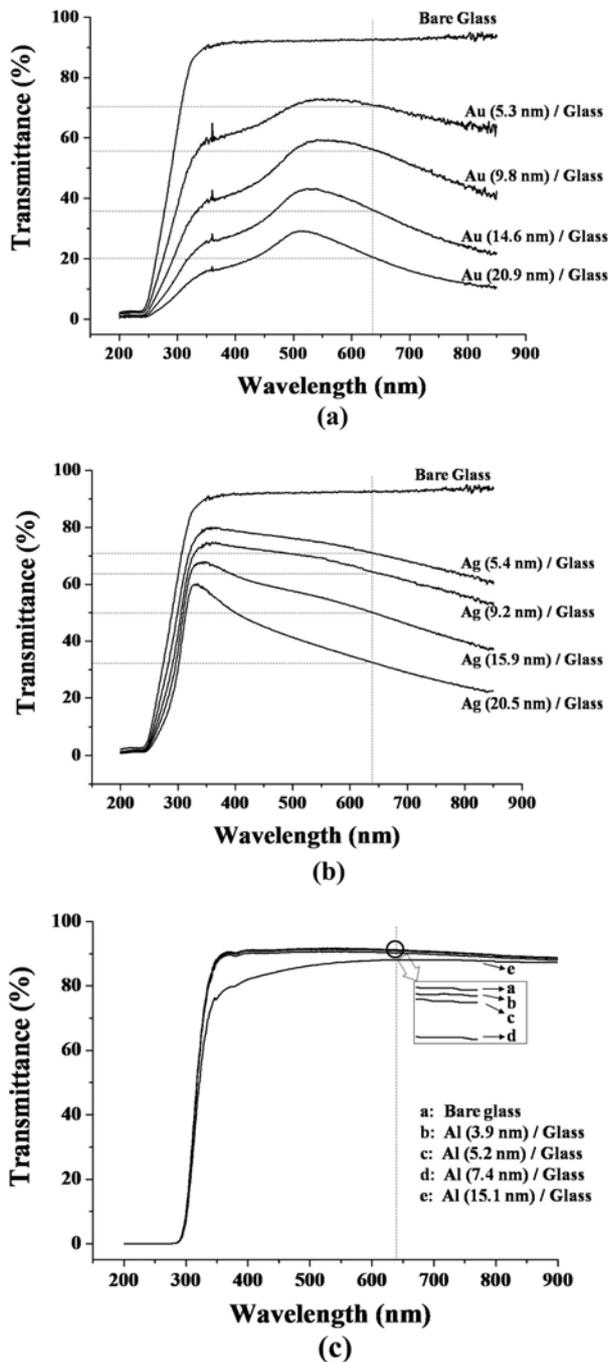


Fig. 2. The transmittance spectra of Au/glass, Ag/glass, and Al/glass samples with different Au, Ag, and Al film thicknesses, along with that of a glass sample, respectively.

PL enhancing effect of Au passivation may be partly ascribed to this high oxidation-resistance of Au. This property of Au made it popular as a jewel, but seems to be unfavorable for the purpose of the passivation of PS.

The FTIR spectra of Al/PS samples with different Al film thicknesses are shown in Fig. 3. The broad absorp-

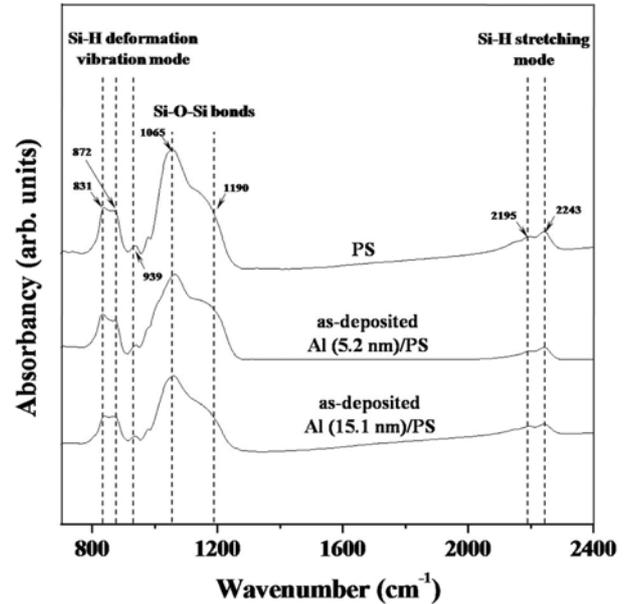
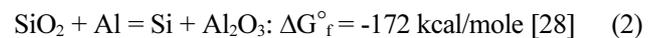


Fig. 3. The FTIR spectra of Al/PS samples with different Al film thicknesses.

tion band appearing between 900 cm^{-1} to 1240 cm^{-1} with its peak at 1065 cm^{-1} is associated with Si-O-Si bonds [14]. The FTIR spectra demonstrate that the intensity of the absorption band for the Si-O-Si bonds decreases by depositing an Al film 5.2 nm thick on the PS. Native oxides exist at the surface of PS due to the reaction between Si atoms at the PS surface and oxygen molecules in air, the so-called natural oxidation. The Si-O-Si bonds must originate from these native oxides on the PS surface. If the PS surface is passivated with a thin Al film, the following reaction will spontaneously occur at room temperature:



The native oxides will be reduced to Si atoms and the Si atoms will create bonds with Al atoms. Therefore, we may conclude from the above discussion that enhancement in the PL intensity of PS by depositing a 5.2 nm Al film on the PS is related to the decreases in the number of Si-H and Si-O-Si bonds and the increase in the number of Si-Al bonds. If the unstable Si-H bonds and Si-O-Si bonds at the PS surface react with Al atoms in the Al film to form stable Si-Al bonds, the concentration of non-radiative recombination centers such as surface states and oxide charges will decrease. As a result of this change in the Si bonding state, the PL of the PS will be enhanced by deposition of a 5.2 nm Al film. In contrast, there are nearly no change in the Si bonding state from the Si-O-Si bond to the Si-Au bond in the PS passivated with a thin Au film.

4. CONCLUSION

The influence of ultrathin metal film passivation by using RF magnetron sputtering on the PL from PS has been investigated. It has been found that Ag passivation is the most effective in enhancing the PL of PS among Ag, Au, and Al, primarily due to the high electrical conductivity of Ag. In contrast, it appears that Au passivation is the least effective in enhancing the PL of PS, primarily because of the high oxidation resistance and low optical transmittance of Au. Al shows a PL enhancing effect higher than that of Au in spite of its lower electrical conductivity than that of Au. The higher PL enhancing effect of Al seems to be due to its higher optical transmittance than that of Au. The PL enhancing mechanism in Al has also been discussed with the aid of FTIR analysis results.

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