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Properties of chemically deposited Cu_2S films on porous silicon

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The electrical and optical properties of Cu_2S films, deposited on porous Si from a chemical bath, are presented. Annealing of the deposited film in air, at an optimized temperature of 150 °C, is shown to be essential to get films with the lowest values of electrical resistivities. The film is more than 60% transparent in the wavelength range of 600–1200 nm. Films deposited on porous Si produce Schottky-like diodes. The best diode characteristics are obtained after annealing the film at 150 °C. The diodes show both photoresponse and electroluminescence properties. Luminescence from porous Si, with a top coating of annealed Cu_2S, is about 70% of that obtained when no coating was applied. © *1997 American Institute of Physics.* [S0021-8979(97)07413-6]

I. INTRODUCTION

Formation of stable rectifying junctions with porous silicon (PSi),[1] with good forward and reverse characteristics, is one of the most challenging problems for the proper exploitation of the material in the device industry. Vacuum deposited Au (Refs. 2–4) and Al,[5] sputter-coated indium tin oxide,[6,7] and conducting polymers[8,9] have been used with limited success for fabricating light-emitting diodes and photodetectors. We have recently shown that an electroless deposition of Ni on PSi, from an aqueous solution, gives significantly better rectifying or Ohmic contacts due to the filling of the pores by the deposited metal.[10,11] Deposition of a film by a similar technique, which is both electrically conducting and optically transparent, could lead to the fabrication of improved PSi based photodiodes and electroluminescent devices. In a recent work,[12] a technique has been described for the deposition of conducting chalcogenide films on glass from an electroless plating bath. A variety of chalcogenide materials having different electrical conductivities and optical transmission characteristics have been reported. Out of them, the material Cu_2S looked most attractive for applications over PSi, due to its reported high electrical conductivity and 50%–70% optical transparency in the emission wavelength band of PSi. We have deposited this film on PSi and optimized and characterized its properties. This work is being presented in this paper.

II. FILMS ON GLASS

About 0.1 μm thick film of Cu_2S was deposited from a bath,[12] containing 8–10 ml of 0.5 M $CuSO_4$ solution and an equal volume of 1 M $Na_2S_2O_3$ solution. Deionized water was added to this to make a total volume of 80–100 ml. Films were deposited on clean corning glass sheets whose surfaces were activated by a 2 min immersion in 0.03% $SnCl_2$ solution. Deposition was done for 30 min in the temperature range of 40–45 °C. After deposition, the glass sheets were cut into several rectangular pieces and some of them were annealed in air for 10 min at temperatures of 50, 100, 150, and 200 °C.

Electrical resistivities of the as-deposited and the annealed Cu_2S films were measured by a four-terminal method, using evaporated aluminum contact strips. Figure 1 shows the resultant film resistivity, plotted as a function of annealing temperature. Resistivity of the film, measured before annealing, is also presented in Fig. 1 for comparison. The parameter decreased sharply as the temperature of annealing is increased and attained a minimum value of $3.5 \times 10^{-4}\ \Omega$ cm after anneal at 150 °C. This value is more than one order of magnitude lower than that obtained previously.[12] Any change in the crystalline structure of the films due to annealing may be ruled out in view of the earlier reports,[12] and we believe that the observed decrease in film resistivity resulted from a corresponding reduction of the moisture content of the film during annealing. The drastic increase in resistivity after the 200 °C anneal may be attributed to a partial oxidation of the Cu_2S film in air.

Optical transmission spectra for the as-deposited and the 150 °C annealed films were recorded in a CARY 5 UV-VIS-NIR spectrophotometer. A clean glass sheet was placed in the reference beam so that only the film characteristics were obtained. The resultant data are being shown in Fig. 2. The transparency of the as-deposited film is above 60% in the wavelength range of 600–1200 nm. Maximum transmittance of 75% is obtained at 800 nm and the parameter falls to about 68% at the 1000 nm wavelength. There is a marginal change in the transmission characteristics of the film after annealing, where the maximum transmittance is reduced to around 73% and the transmittance in the longer wavelength region is slightly increased.

III. FILMS ON POROUS Si

The anodic etching technique, used for forming PSi in our laboratory, has been described earlier.[11] The Si substrates, used in this study, were *n* and *p* type, oriented in the ⟨111⟩ and the ⟨100⟩ directions, respectively. In all cases, the thickness of the PSi layer was about 10 μm.

Cu_2S films, 0.1 μm thick, were deposited directly on PSi without any $SnCl_2$ activation. In order to study the electrical behavior of the Cu_2S/PSi contact, we deposited the film on PSi, formed on 1 Ω cm *p*-type Si substrates. Next, 3 mm diam mesa structures were defined on the sample using black wax masks and a suitable Si etchant, which cut through both the film and the PSi region. Electrical contact to the film surface was made by a thin gold wire probe. The Al metal-

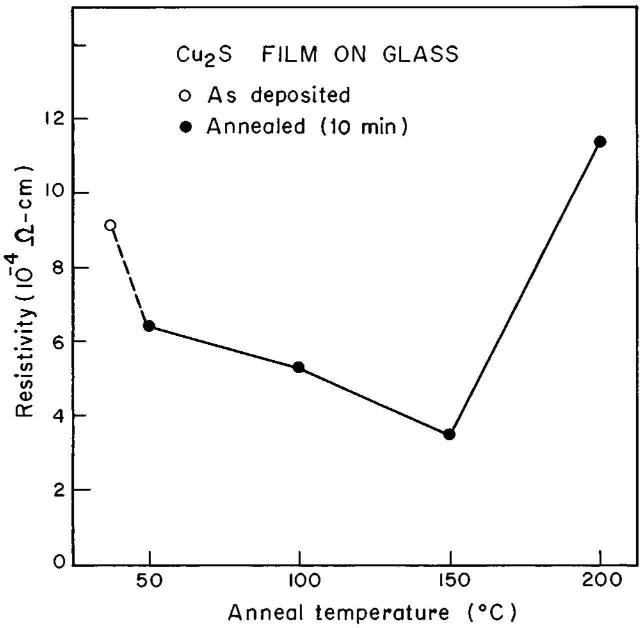

FIG. 1. Resistivity of the as-deposited and the annealed Cu_2S films on glass.

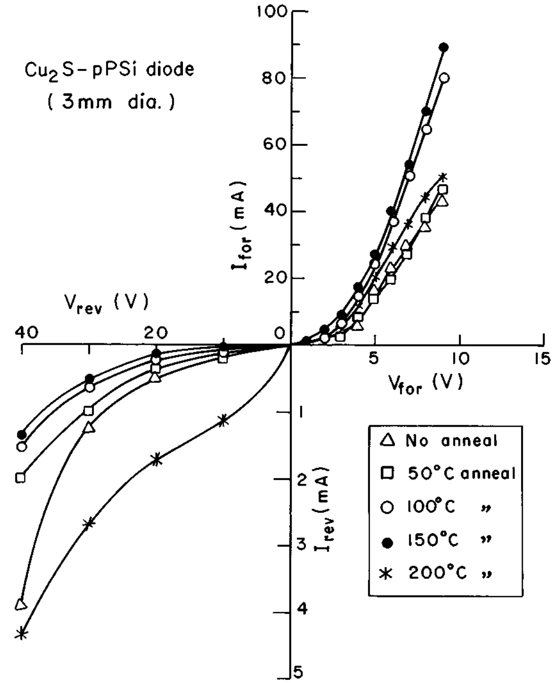

FIG. 3. $I-V$ characteristics of Cu_2S–p-type PSi diodes. The data for devices using as-deposited Cu_2S film as well as films annealed at different temperatures are being shown.

lization on the back surface of the substrate, which was made before PSi formation, served as the other contact. The current–voltage ($I-V$) characteristics of the device, shown in Fig. 3, resemble that of a metal–semiconductor Schottky diode with a reverse breakdown voltage above 20 V. In an attempt to improve the characteristics of this diode, the Cu_2S coated PSi samples were annealed in air for 10 min at temperatures of 50, 100, 150, and 200 °C. The $I-V$ characteristics of the mesa diodes, fabricated on the annealed structures are being shown in Fig. 3. Annealing shows a continuous improvement of the diode properties up to 150 °C and then degradation occurs. The diode fabricated on the 150 °C annealed structure has a rectification ratio around 1000 and a measured ideality factor of 2.5. Under forward bias, the diode exhibited orange-green electroluminescence, which was observed even in semidark rooms. Further, the diode showed strong photoresponse under normal room illumination. The work on the electroluminescence properties of the Cu_2S–PSi diodes will be presented in a future publication. We report below on their photoresponse properties.

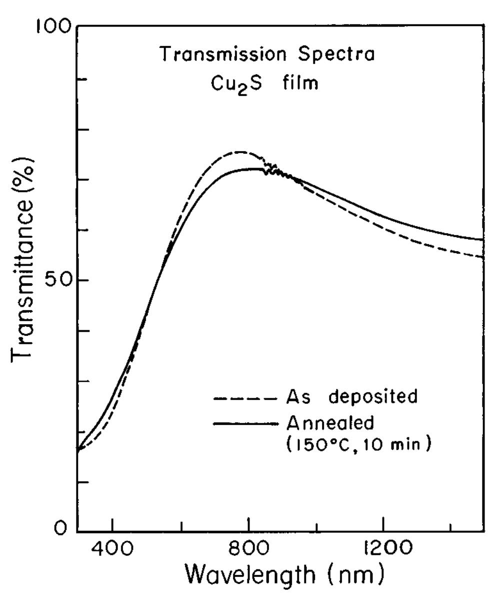

FIG. 2. Optical transmission spectra for the as-deposited and the 150 °C annealed Cu_2S films.

The test devices were 1.5 mm diam mesa diodes fabricated on 150 °C annealed Cu_2S–PSi layer structures. The substrates were both n and p type having resistivities of 50 and 40 Ω cm, respectively. The reverse $I-V$ characteristics of the diodes were first tested in the dark and then the experiment was repeated by shining the film surface with light from a 60 W tungsten filament lamp, placed 20 cm apart. Figure 4 shows the results. For the diode, fabricated on the n-type sample, the increase in reverse current is about ten times under illumination. The dark reverse current for the diode on p-type PSi is about 500 nA at a reverse voltage of 20 V. More than 20 times enhancement of this current is observed after exposure to light. Hence, the system may act as an excellent candidate for making high efficiency photodiodes.

Finally, we tested the optical emission from PSi, through Cu_2S film, in a Perkin Elmer model MPF-44B fluorescence spectrometer. PSi, formed on p-type Si, was used in the experiment. Excitation was provided at a 350 nm wavelength and the luminescence from the material was detected in a photomultiplier and recorded as a function of emission wavelength. The emission from a bare PSi surface, as well as that from the PSi surface coated with either as-deposited or

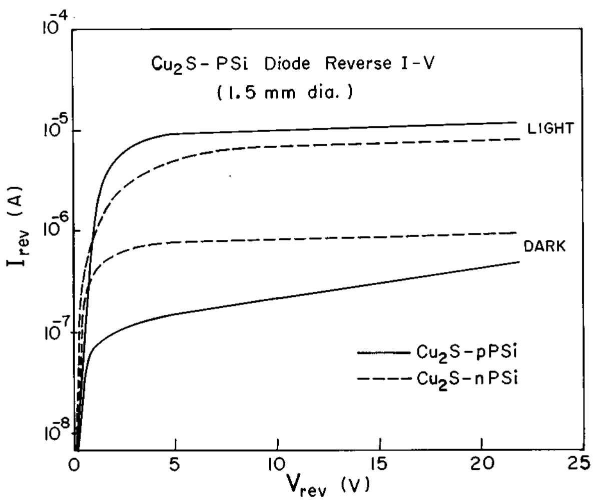

FIG. 4. Reverse $I-V$ data for Cu_2S–PSi diodes in the dark and in the presence of light. Si substrate resistivity for p- and n-type PSi are 40 and 50 Ω cm, respectively.

150 °C annealed Cu_2S film, was recorded. The resultant emission spectra are being shown in Fig. 5. The intensity of luminescence from PSi reduced to about 38% of its original value after the surface was covered with as-deposited Cu_2S. Annealing of the film, on the other hand, increased the luminescence to about 70% of that from the uncoated PSi surface. This almost twofold increase in luminescence through the Cu_2S film cannot be attributed to an improvement in the transmittance of the film, as per our experimental data in Fig. 2. The other possibility is a change in the structure of PSi after 150 °C anneal. We have checked for it by first annealing the PSi sample alone in air at 150 °C and then recording the luminescence from the porous surface with or without a top Cu_2S layer. These data are being shown by the dotted curves in Fig. 5. There is a fall in luminescence from PSi after annealing. This result is in agreement with the earlier observations of the decrease in luminescence intensity from PSi after low-temperature oxidations.[13] Further, we note that the annealing of PSi alone does not have any effect on increasing luminescence through Cu_2S. It is then the annealing of the Cu_2S–PSi interface that is important. The possible effect of such annealing may be the removal of water microparticles that are trapped at the interface and attenuate the light emitted from PSi.

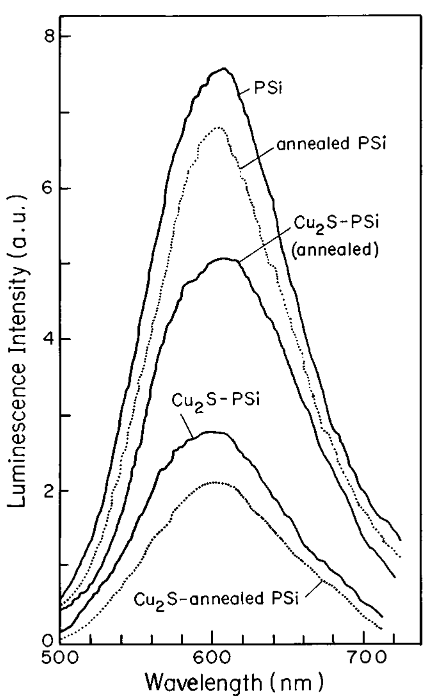

FIG. 5. Luminescence from PSi through a top film of Cu_2S, compared with that from a bare PSi surface. Data for materials prepared under different conditions, as indicated in the figure, are presented.

IV. CONCLUSION

We have developed a technique for depositing thin transparent conducting films of Cu_2S on porous Si from a chemical bath. An annealing procedure has been optimized to get films with electrical resistivity as low as 3.5×10^{-4} Ω cm. The optical transparency of the film is above 60% in the wavelength range of 600–1200 nm with a peak transmittance of 75% at 800 nm. A similar annealing procedure has been developed to improve the rectifying characteristics of the film–PSi junction. Cu_2S–PSi diodes exhibit strong photoresponse under reverse bias and electroluminescence under forward bias. Annealing is also shown to be essential to improve luminescence from the PSi surface through a top coating of Cu_2S.

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