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Semitransparent Metal-Si Electrodes for a-Si:H Photodiodes and Their Application to a Contact-Type Linear Sensor Array

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It has been found that thin mixed metal-Si layers formed through solid state reaction between hydrogenated amorphous silicon and metals can be used as semitransparent electrodes. By the use of these layers, metal interconnection and semitransparent electrodes can be formed simultaneously, which results in a greatly simplified device fabrication process. A linear sensor array using a Cr-Si layer has been successfully developed. The fabricated sensor has as good characteristics as that using ITO.

1. Introduction

Recently, integrated image sensors using hydrogenated amorphous silicon (a-Si:H) have been extensively studied.[1-4] In such devices, R.F. sputtered semiconductive oxides, e.g., ITO, In_2O_3 or SnO_2, are widely used as the transparent electrodes. However, these oxides cause sputtering damage to the surface of the a-Si:H. Moreover, these oxides dissolve in many kinds of acid. This increases the complexity of fabricating integrated image sensors. Therefore, a transparent electrode that is chemically stable and does not degrade the characteristics of a-Si:H is strongly desired.

It has been found that various silicides or metal-Si intermixing layers can be formed as a result of the solid-state reaction between a-Si:H and metals.[5,6] Through our work on the metal-Si interface reaction, we have found that such interface layers that are very thin can be used as semitransparent electrodes. Many different metals, for example, Cr, Ni, Mo, Pt, or Pd, can be employed as source materials.[7]

This paper describes fabrication and testing of a Cr-Si layer and it's application to a linear sensor array.

2. Fabrication and Analyses of Semitransparent Electrodes

The fabrication process for this Cr-Si layer is as follows. An a-Si:H film is deposited by R.F. glow-discharge decomposition of SiH_4 on the glass substrate. Deposition is carried out at a substrate temperature of 230°C and an atomospheric pressure of 1.0 Torr. Cr is then vacuum evaporated on top of the a-Si:H film without substrate heating. The thickness of Cr film is about 50 nm. After annealing, the residual Cr film is etched off in $(NH_4)_2Ce(NO_3)_6$ 250 g/l solution. This forms a Cr-Si layer on the a-Si:H surface. Reproducibility of the characteristics of the Cr-Si layer is provided by surface treatment in a $HF:HNO_3:H_2O$ (1:1:30) solution before deposition of the Cr.

The sheet resistance of such a layer annealed at 200°C for 30 min is about 10 kΩ/□. The transmittance of this layer was estimated from the transmittance values obtained before and after formation of the layer on a-Si:H film of various thicknesses. The result is shown in Fig.1.

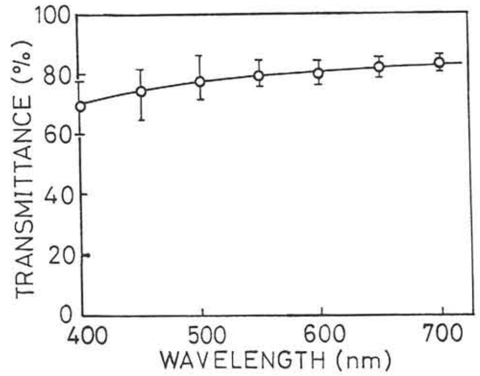

Fig.1 Transmittance of Cr-Si layer

Cr-Si layer thus produced was analysed by IMA (ion micro analysis). The spectra for a sample with an as-deposited Cr (solid line) and for samples from which the metal layers were removed (broken lines) are shown in Fig.2. These samples were prepared using different heat treatments. The parameter is the sheet resistance of these layers. From this figure, the thickness of these layers can be estimated to be less than 10 nm. This estimation was supported by RBS measurements. Another experiment was performed to evaluate the thickness of this layer. A thin layer of a-Si:H was deposited onto the glass substrate and then Cr was evaporated and annealed under the condition described above. The Cr was then removed, and the sheet resistance was measured. The measured resistance was found to be constant in a-Si:H films thicker than 5 nm. However, for a-Si:H thinner than 5 nm, the resistance increased abruptly. This suggests that the Cr-Si layer thickness is about 5 nm.

IERS (interference enhanced Raman scattering) measurements[5] were conducted to determine the structure of this layer. Measured IERS spectra of 5nm thick layers are shown in Fig.3. From this figure, it was found that typical peaks of a-Si:H disappeared due to formation of the Cr-Si layer. On the other hand, the spectrum of Cr-silicide formed on crystalline Si by heat treatment at 800 °C for 2 hrs shows strong peaks at 115 cm^{-1} and 75 cm^{-1}. Therefore, it is assumed that this layer is not silicide but an intermixing phase .

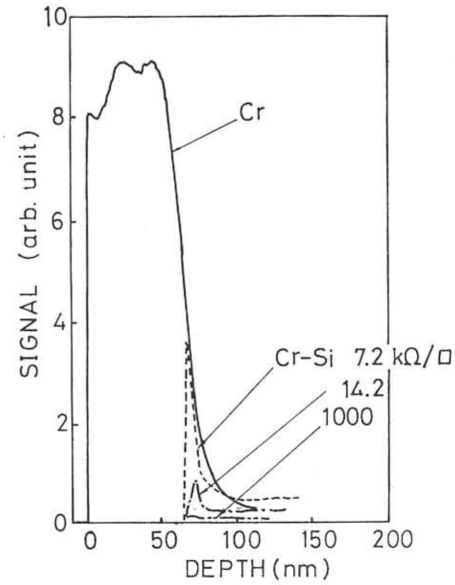

Fig.2 IMA spectra of a-Si:H/Cr system

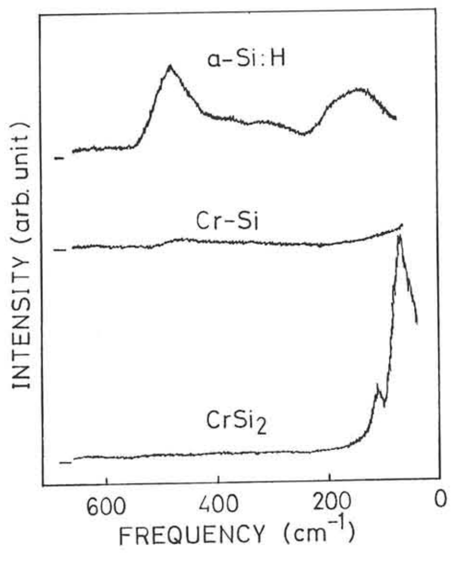

Fig.3 Raman spectra

This Cr-Si intermixing layer is very stable under various treatments. Table 1 shows the sheet resistance change when this layer is dipped in various solutions and exposed to oxygen plasma. It dissolves only in HF solutions.

These results indicate that this layer can be used as a semitransparent electrode in a-Si:H devices. We therfore used this layer in a linear sensor array.

Table 1 Stability of Cr-Si layer

Treatment		t(min)	$\Delta\rho_s/\rho_s$(%)
H_3PO_4	conc.	5	0
H_2SO_4	30%	5	<2
HCl	conc.	5	0
HNO_3	conc.	5	<2
NaOH	10%	5	0
$HF:HNO_3:H_2O$(1:1:30)		5	∞
J-100	100 °C	5	0
O_2plasma	200W	5	15
		20	15
		40	45

3. Device Structure and Fabrication

The fabricated sensor was a 512-bit (8 bit/mm) photosensor array with an overall length of 64 mm. Figure 4 shows the equivalent circuit configuration of this sensor. In order to derive the matrix configuration, each a-Si:H pin photodiode was connected in series, and in reverse direction to a blocking diode.

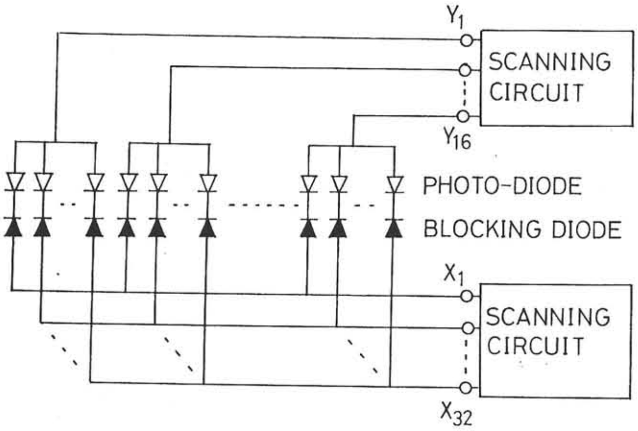

Fig.4 Equivalent circuit configuration for the fabricated sensor

The schematic cross-section of this sensor is shown in Fig.5. The fabrication procedures were as follows. First, 0.2 µm thick Cr electrode stripes were formed on a 30 mm by 75 mm glass substrate. Next, a-Si:H film was deposited to a total thickness of 0.6 µm with the n-layer first, followed by the i-layer and p-layer. The thickness of each layer is 0.03, 0.55, 0.02 µm respectively. This a-Si:H film was patterned photolithographically to 100x130 um^2 by dry etching using CF_4 gas. Then, a 2 µm thick SiO_2 film was formed by R.F. sputtering. This served both as a cover to prevent the a-Si:H edge portion from shorting out, and as an insulator for double layer interconnection. Contact holes were then formed in this SiO_2 layer. After photoresist stripping, the sample was immersed in a $HF:HNO_3:H_2O$ solution to remove native oxide on the a-Si:H surface. Then, a double layer of Cr/Al was deposited at a pressure of about 10^{-6} Torr by vacuum evaporation using a tungsten foil source. The Cr and Al were 50 nm and 1.5 µm thick, respectively. The sample was then annealed at an ambient temperature of 200 °C for 30 min to form the Cr-Si layer on the surface of the a-Si:H diodes. The double layer of Cr/Al was photoetched in a H_3PO_4-HNO_3-H_2O solution for the Al, and in an $(NH_4)_2Ce(NO_3)_6$ solution for the Cr. In this step, the metal interconnection and semitransparent electrode were formed simultaneously. This resulted in a greatly simplified sensor fabrication process. Then, a 2 µm thick Si_3N_4 layer was deposited as the antireflection layer. This Si_3N_4 layer also served as the passivation layer. A microscopic view of this sensor is shown in Fig.6.

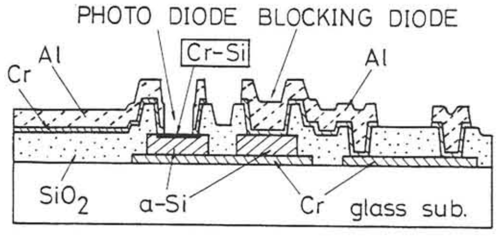

Fig.5 Cross-section of the fabricated sensor

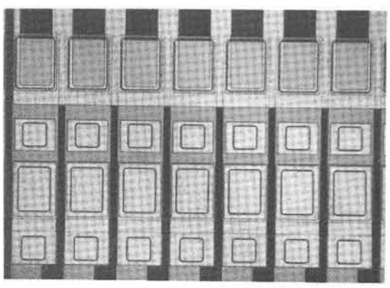

Fig.6 Microscopic view of the fabricated sensor

4. Device Characteristics

The spectral sensitivity of the photodiode at a reverse-bias of 2 V is shown in Fig.7. For comparison, the spectral response of a photodiode with an ITO transparent electrode is shown in the same figure. As shown, the spectral responses of these two samples are almost the same.

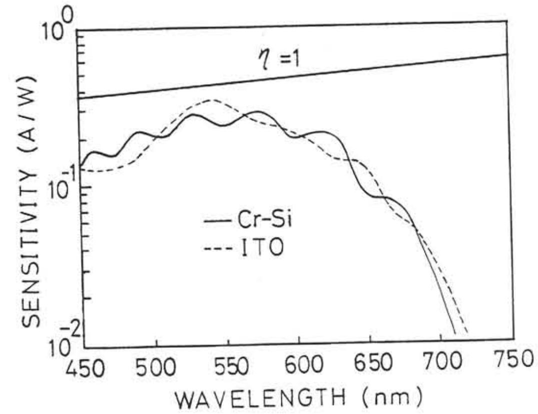

Fig.7 Spectral Sensitivity of the photo-diodes

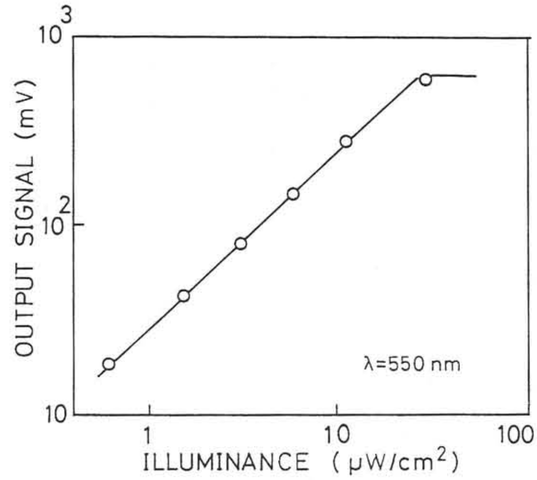

Fig.8 Photoelectric conversion characteristics of the fabricated sensor

As for I-V characteristics, the diode with the Cr-Si electrode has better forward bias characteristics than the diode with the ITO electrode. The n value (ideality factor of the diode) for the forward current of the Cr-Si electrode diode is about 1.2, while that for the ITO diode is about 2. As for reverse bias, little difference between the Cr-Si electrode diode and the ITO diode is observed.

The photoelectric conversion characteristics are shown in Fig.8. The measured γ values are nearly equal to unity. The read out time per pixel for the fabricated sensor is 2.23 μs/bit, so it is possible for this sensor to read an A4 size document at a speed of less than 5 ms/line. The S/N ratio is about 28 dB. The amplitude response at 8 lines/mm is about 66 %. These characteristics did not show any changes during a 500 hr. drive test or in a heat cycle test of 200 cycles between -30 ℃ and 120 ℃. These results are almost the same as those for the sensor with the ITO electrode.[1)]

5. Conclusion

A linear sensor array that uses a Cr-Si layer as a semitransparent electrode has been developed. The use of this layer greatly simplifies the sensor fabrication process.

The resistivity of this layer is about 10 kΩ/□. The thickness and the transmittance have been estimated to be about 5 nm and 80 %, respectively. A photodiode using this layer has almost the same sensitivity as a photodiode using an ITO electrode. It has also been confirmed that this layer is stable enough to be used as the transparent electrode in practical devices.

These results imply that this Cr-Si layer is applicable to other devices, such as solar cells and TV image pickup devices.

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