JOURNAL OF MATERIALS SCIENCE **38** (2003) 917–920

Electrical characteristics of Cu-PS-Si structures

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The effect of ambient humidity on the current-voltage characteristics of Cu-PS (porous silicon) structure was investigated. The humidity-voltaic effect, i.e. the generation of open-circuit voltage (V_{oc}) in Cu-PS interface in humid atmosphere (up to 300 mV at 95% relative humidity) in dark and day-light illumination is discovered. Humidity-stimulated open-circuit voltage generation is caused by hydrogen component of water-vapor of ambient. The possible mechanism of hydrogen-stimulated voltage generation in Cu-PS interface is suggested. Besides this effect, annealing in the range of 60–200°C in air on V_{oc} of Cu-PS structures was studied and decrease of values of V_{oc} depending on duration of annealing was discovered. These changes were attributed to diffusion of oxygen from air and oxidation of copper film. ($V_{oc} - t$) data were used for estimation of diffusion coefficients of oxygen in Cu film. The temperature dependence of the oxygen diffusion coefficient in Cu films are described by the relation $D = 5.2 \times 10^{-7} \exp(-0.44/kT)$. The results of this research showed that Cu-PS structures can be perspective for using as hydrogen sensors. © *2003 Kluwer Academic Publishers*

1. Introduction

The discovery that highly porous silicon (PS) could efficiently emit visible light at room temperature has generated an enormous interest in this material in view of its possible use for electronic applications [1]. The structure is characterised by a great number of micropores (2–50 nm in mean diameter) and an extremely large surface area to volume ratio (up to 10^3 m^2/cm^3). PS surfaces are covered by silicon hydrides and silicon oxides. Surfaces bonds, in particular Si—H bonds play an important role in regulating of electrical, optical and other properties due to the large internal surface area of PS. The composition and property changes of PS caused by hydrogen and oxygen diffusion are rarely considered [2–4]. The porosity of crystalline structures opens new perspectives using of metal-PS structures as gas sensors.

It is worth noting that the environment exerts the influence on photoluminescence and electrical characteristics of PS and metal-PS structures. The presence of water-vapour environment causes Si—Si bond breaking with formation of Si—H bonds [5]. Balagurov *et al.* [6] analysed the influence of water-vapour environment on the photoluminescence spectrum of PS. Hydrogen detection with palladium modified PS was studied by Polyshchuk *et al.* [7]. In Au-PS surface type structure, Yamana *et al.* [8] discovered the dependence of the current on the relative humidity (RH) under applied voltage. Taliercio *et al.* [9] suggested to use PS films as efficient membranes of oxygen sensors. Oxidised porous silicon has been presented as a novel and a promising substrate material for biosensors [10]. The over-Nernstian potentiometric response of PS devices towards sodium ions have been reported [11, 12].

The humidity-voltaic effect, i.e. the generation of open-circuit voltage in Ag-PS structure in humid atmosphere is discovered and on the important role of the upper metal have been indicated [13, 14]. Both Cu and Ag metal are elements of one group and are characterised by the close work functions. Therefore, there is reason to believe that also Cu-PS structure (like Ag-PS structure) shall show humidity-sensitive properties. In this work humidity-sensitive characteristics of Cu-PS-Si structures have been examined.

2. Experimental procedure

The PS layers on Si substrates were prepared by anodic etching in a solution $HF:H_2O = 1:3$ at a d.c. current of 15 mA/cm^2 under the white light illumination. n-type Si (111) monocrystalline wafers of resistivity $\rho = 1 \times 10^{-2}$ Ω cm are used as the substrates. In some runs PS layers were detached from Si substrates by electropolishing under former solution with a current density of 0.8–1.0 A cm^{-2}. PS layers on Si substrates and free-standing layers were characterised by porosity and thickness measurements. PS layers of thickness 10–20 μm and porosity 70–80% were analysed in this work.

For current-voltage measurements, the ohmic indium contact was deposited on the back (Si) surface of PS-Si structures. The Cu-PS-Si structures have been fabricated by evaporation of Cu film (by thickness 30–40 nm) onto the PS surface at room temperature using electron-beam evaporation technique. The thickness of Cu films was measured during evaporation by using Deposition Controller (Inficon, Leybold). Indium or In-Ga alloy was used as ohmic contact to PS layers. Current-voltge characteristics and humidity-stimulated the open-circuit voltage (V_{oc}) generation in Cu-PS, Cu-PS-Si and PS-Si structures were examined at room temperature (295 K) in the measuring cell at different ambient humidity (water vapour or oxygen). The relative humidity (RH) in cell was measured by using 'Extech-444701' Hygro-Thermometer.

The photosensitive properties of Cu-PS-Si structures were analysed by measurements of I-V characteristics in dark, day-light and under illumination by a tungsten-halogen lamp (150 mW cm^{-2}). All investigated Cu-PS, Cu-PS-Si and PS-Si structures showed very slight photosensitiveness. Therefore, most of measurements have been performed at day-light illumination.

For examination of the effect of the heat treatment on I-V characteristics and humidity-stimulated changes of the open-circuit voltage of Cu-PS-Si structures, samples were exposed to sequential annealings in air or in vacuum (about of 1.3 Pa) at fixed temperature (60, 100, 150 or 200°C) and measurings of V_{oc} at room temperature (at 80% RH). Then open-circuit voltages in depending on duration of annealing data ($V_{oc} - t$ curves) were used for the estimation of the oxygen diffusion coefficient in Cu film.

3. Results and discussion

I-V characteristics of Cu-PS-Si in dark and illumination (150 mW cm^{-2}) at the normal room conditions (45% RH and $T = 295$ K) are presented in Fig. 1. It is seen that I-V characteristics of Cu-PS-Si structure show the rectifying properties. Herewith the values of current under 'forward' voltages (the positive polarity on Cu film) are larger than those for 'reverse' voltages. The I-V characteristics of Cu-PS-Si structure is slightly sensitive to illumination. The values of forward currents under illumination are increased by about 5% and photostimulated open-circuit voltage is about 1–2 mV. It is noted that from investigated three types structures (Cu-PS-Si, Cu-PS and PS-Si structures), Cu-PS-Si and Cu-PS-structures showed approximately the same rectifying I-V characteristics, while I-V characteristics of structures without Cu film (PS-Si structure) were close to ohmic. Besides the rectifying properties of both Cu-PS-Si and Cu-PS in equal degrees depended on ambient humidity, while I-V characteristics of PS-Si structures were slightly sensitive to ambient humidity.

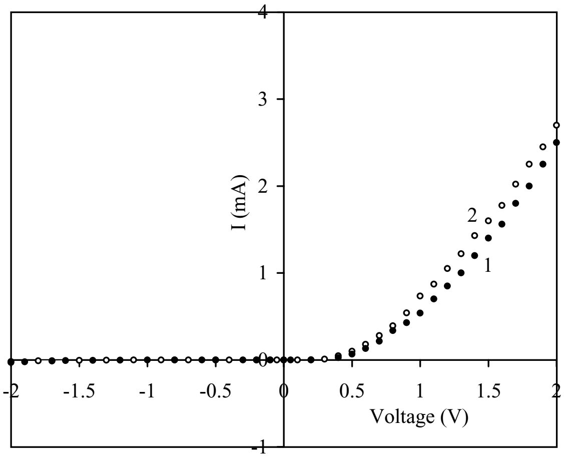

Figure 1 The I-V characteristics of Cu-PS-Si structure in (1) dark and (2) under illumination (150 mW cm^{-2}).

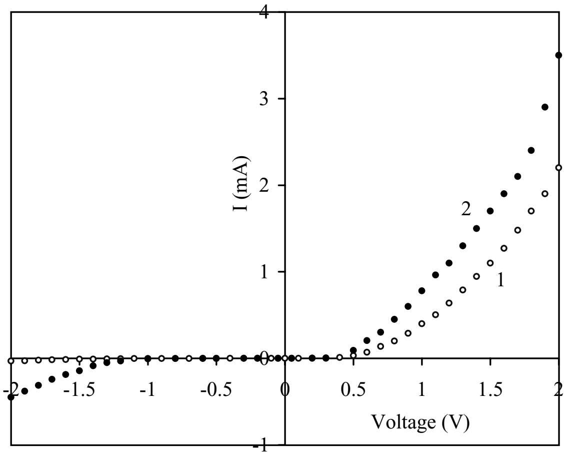

Figure 2 The I-V characteristics of Cu-PS-Si structure in air ambient (1) 45% RH and (2) 80% RH.

The typical I-V characteristics of Cu-PS structure in air ambient at 45% RH and 80% RH (295 K) are presented in Fig. 2. As seen from Fig. 2 the forward and the reverse currents considerably increase with rise of the relative humidity. The forward and reverse currents ($V = \pm 2$ V) at the relative humidity 80% RH increase by factor 1.5 and 7 respectively in comparing with those at 45% RH.

The humidity-voltaic effect, i.e. the generation of open-circuit voltage under humidity exposition is discovered for both Cu-PS-Si and Cu-PS structures. This effect was not observed in structures without copper film (PS-Si). Fig. 3 illustrates the open-circuit voltage in dependency on the relative humidity for one of such the Cu-PS structures. It is seen that the open-circuit voltage approximately linearly increases from 30 to 300 mV with rise of the relative humidity from 50% RH to 95% RH. The humidity-sensitivity of the Cu-PS sensor is about of 6 mV/%RH and response time is about 2–3 s.

Measuring of I-V characteristics of Cu-PS structures under pure oxygen gas exposition did not show the oxygen-stimulated changes of I-V characteristics or generation of noticable value of open-circuit voltage. These results suggest that humidity-stimulated changes

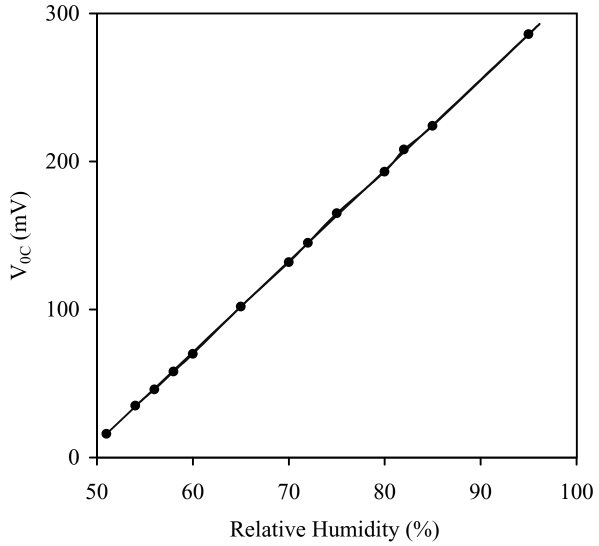

Figure 3 The open-circuit voltage-relative humidity dependence for Cu-PS structure.

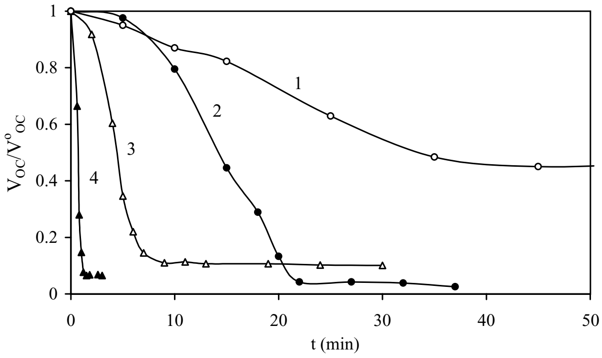

Figure 4 The open-circuit voltage (80% RH)-annealing duration curves of Cu-PS structures exposed to annealing in air at (1) 60°C, (2) 100°C, (3) 150°C and (4) 200°C.

of electrical characteristics of Cu-PS structures are mainly caused by hydrogen.

Data on the effect of duration of annealing of Cu-PS structures in air atmosphere at 60°C, 100°C, 150°C, and 200°C on values of V_{oc}/V^{o}_{oc} at 80% RH (here V^{o}_{oc} is the open-circuit voltage before annealing, for $t = 0$) are presented in Fig. 4. It is seen that for all temperatures the increase of duration of annealing is accompanied at first by decrease and then by saturation of the open-circuit voltage. Herewith, the rate of decreasing of V_{oc} increases with raising of annealing temperature from 60°C to 200°C. Long-term stability measuring of open-circuit voltage at room temperature in air showed that the V_{oc} at first 5–7 hours decreased up to about of 0.9 V^{o}_{oc} and then next 5 month very weekly changes. These experiments are continued. Possible explanation related with the oxidation of the upper Cu film of Cu-PS structure during annealing in air suggests themselves for these runs.

Data on open-circuit voltage at 80% RH of Cu-PS structure exposed to annealing in vacuum (1.3 Pa, $T = 150$°C) depending on duration of annealing are shown in Fig. 5. The very slight decrease of values V_{oc} with duration of annealing in vacuum in comparison to that for annealing in air (Fig. 4) is observed.

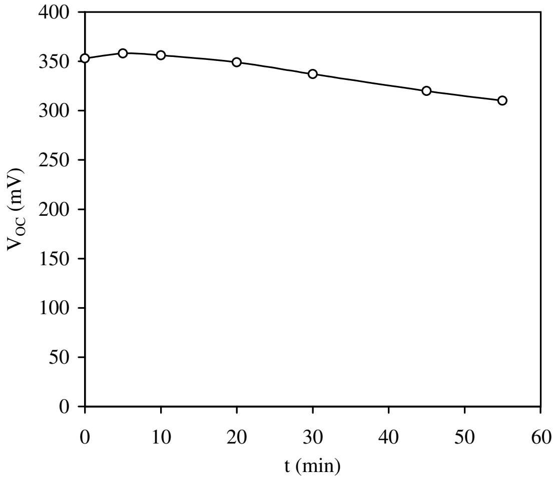

Figure 5 The open-circuit voltage (80% RH)-annealing duration curve of Cu-PS structure exposed to annealing in vacuum (1.3 Pa) at 150°C.

Thus, the next experimental results related with humidity-stimulated changes of electrical characteristics of Cu-PS structures are established: (1) Humidity-stimulated effects (changes of I-V characteristics and generation of open-circuit voltage) are observed in Cu-PS-Si and Cu-PS structures, whereas for PS-Si structures (without Cu film) these effects are very slightly expressed. (2) Value of open-circuit voltage linearly increases with rise of the relative humidity. (3) Changes of electric characteristics of Cu-PS structures and generation the open-circuit voltage of marked value were not observed under oxygen exposure. (4) Cu-PS structures are very weakly sensitive to illumination (open-circuit photovoltage is about 1–2 mV under illumination of 150 $\mathrm{mW\,cm^{-2}}$). (5) Annealing of Cu-PS structures in air is accompanied by decrease of $V_{oc,}$ whereas such decrease of V_{oc} is not observed on annealing in vacuum.

For Cu-PS structures just as Ag-PS structures [14] about mechanism of humidity-stimulated changes of I-V characteristics and generation of the open-circuit voltage one can express only speculative suggestions. The Cu film on the PS surface plays two-fold roles. The Cu film is membrane material which transmits small hydrogen atoms or ions and it is the component of a Cu-PS Schottky-type contact. If hydrogen is accepted as a donor impurity in PS [15], then adsorption and dissolution of the water molecules on Cu film due to interaction with the copper surface, penetration of hydrogen ions through Cu film and subsequent reaching the Cu-PS interface is accompanied by separation of charges and origin of the open-circuit voltage.

Data on decrease humidity-sensitive characteristics of Cu-PS structures as result of annealing in air (Fig. 4) may be attributed to the oxidation of copper film, so far as such decrease of V_{oc} was observed for structures annealed in vacuum (Fig. 5). Formation of CuO_2 in the near-surface region of Cu film due to oxygen diffusion during annealing of Cu-PS structures in air must hinder the diffusion of H ions. Herewith, the concentration of hydrogen ions at Cu-PS interface shall decrease with increase thickness of growing CuO_2 film. In short, thickness of CuO_2 layer in Cu film is determined by

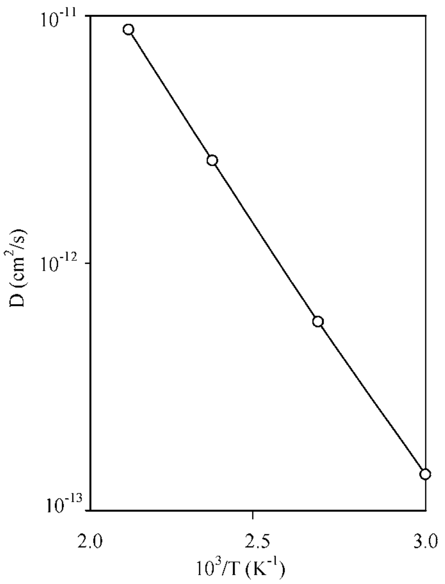

Figure 6 The temperature dependence of oxygen diffusion coefficient in Cu film.

diffusion coefficient of oxygen in Cu film. This suggests that diffusion of hydrogen into Cu film and thereby concentration of hydrogen ions at Cu-PS interface (i.e. value of open-circuit voltage V_{oc}) is limited by effective diffusion coefficient of oxygen in Cu film. For this supposition, the effective diffusion coefficient of oxygen (D) may be estimated from open-circuit voltage-annealing duration curves ($V_{oc} - t$) (Fig. 4) as [16]

$$V_{OC} = Cd(Dt)^{-1/2} \qquad (1)$$

Here d is thickness of Cu layer and C is constant.

The effective diffusion coefficients of oxygen in Cu film of Cu-PS structures for temperature of 60–200°C estimated from Fig. 4 by using Equation 1 were presented in Fig. 6. The temperature dependence of the effective diffusion coefficient of oxygen in Cu films at 60–200°C is described as

$$D = 5.2 \times 10^{-7} \exp\left(-\frac{0.44}{kT}\right) \qquad (2)$$

As is seen from Fig. 6, the diffusion coefficient of oxygen in Cu films in the range of 60–200°C increases from 1.4×10^{-13} to 8.8×10^{-12} cm^2/s. The low value of activation energy of oxygen diffusion in polycrystalline Cu film (0.44 eV) can give evidence migration of oxygen atoms mainly along grain baundaries.

4. Conclusions

Humidity-stimulated changes of I-V characteristics of Cu-PS structures have been established. Formation of open-circuit voltage in Cu-PS structures under ambient humidity (up to 300 mV at 95% RH) was discovered. Generation of V_{oc} is mainly caused by hydrogen component of water-vapor of ambient. Formation mechanism of open-circuit voltage is tentatively attributed to diffusion of hydrogen ions through copper film to Cu-PS interface and successive separation of electrical charges on this interface.

Heat treatment of Cu-PS structures at range of 60–200°C in air results in the decrease of values of V_{oc}, whereas the heat treatment of structures in vacuum is accompanied by slight change of V_{oc}. The changes of V_{oc} due to annealing of Cu-PS structures in air are attributed to oxidation of copper film on surface porous silicon resulting in retarding penetration of hydrogen ions to Cu-PS interface. This data are used for determining diffusion coefficients of oxygen in copper film. The temperature dependence of oxygen diffusion coefficient in Cu films in range of 60–200°C are described by relation $D = 5.2 \times 10^{-7} \exp(-0.44/kT)$.

The results of this research related with the high values of humidity-sensitivity (about of 6 mV/%RH) and linear (V_{oc} − RH) dependence indicate on perspectivity of using of Cu-PS structures as hydrogen sensors.

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Received 20 May
and accepted 5 November 2002