Solid-State Electronics 53 (2009) 663–668

Contents lists available at ScienceDirect

Solid-State Electronics

journal homepage: www.elsevier.com/locate/sse

Stable aluminium ohmic contact to surface modified porous silicon

J. Kanungo, S. Maji, H. Saha, S. Basu *

IC Design and Fabrication Centre, Dept. of Electronics and Telecommunication Engineering, Jadavpur University, Kolkata 700 032, India

ARTICLE INFO

Article history:
Received 29 December 2008
Received in revised form 16 March 2009
Accepted 21 March 2009
Available online 23 April 2009

The review of this paper was arranged by Prof. A. Zaslavsky

Keywords:
Porous silicon
Surface modification
Palladium metal
Ohmic contact
Stability

ABSTRACT

A stable low resistance aluminium (Al) contact to porous silicon (PS) could be achieved by chemically modifying PS surface with palladium chloride ($PdCl_2$) solution. Palladium (Pd) was dispersed over the PS surface by chemical dipping method using very low concentration of $PdCl_2$ solution (0.01 M) and for a very short duration of time (5 s). Field emission scanning electron microscopy (FESEM) was performed to investigate the morphology of the modified PS surface. Digital X-ray image mapping and energy dispersive X-ray (EDAX) spectras were taken to confirm the dispersion and formation of Pd clusters on the porous silicon surface. X-ray photoemission spectroscopy (XPS) confirms that the presence of oxygen is higher in Pd modified porous silicon than that of unmodified one. Aluminium (Al) was thermally evaporated on Pd modified surfaces and the study of *J–V* characteristics showed a linear relationship. Therefore the specific contact resistance (ρ_c) could be measured by transmission line model (TLM) method. Stability of the contact was studied for a time period of around 30 days and no significant ageing effect could be observed.

1. Introduction

Porous silicon has recently attracted scientific and technological attentions for its multifarious applications in sensing and photonic devices [1–6]. The extremely large surface to volume ratio of PS, the ease of its formation, control of the surface morphology through variation of the formation parameters and its compatibility to silicon IC technology leading to an amenability to the development of smart systems-on-chip sensors have made it a very attractive material. But in order to develop porous silicon based devices and their integration to electronic circuits the low resistance stable electrical contacts are necessary. However, unlike crystalline silicon the outstanding problem with PS is to get a stable ohmic contact mainly because of the large surface state density [7].

A few reports are available on the formation of electrical contact to p-type porous silicon. Zimin et al. reported a lateral Al ohmic contact to n-type PS having the contact resistivity of the order of 10^{-3}–$10^{-2}\ \Omega\,cm^2$ for low porosity and low resistivity sample. But for both n- and p-type high resistive PS a rectifying behaviour was observed by them [8]. Martin Palma and co-workers reported the same for the Al–PS–Si–Al sandwich structure, which showed rectifying behaviour even after prolonged exposure to the atmosphere [9]. There are also reports on metallic contacts to PS using Au, In, Au–In, In–Sn, Al, etc. and all the contacts showed Schottky behaviour [10]. Electroless Ni deposition was studied for getting metal contact to PS and an ohmic behaviour was observed only for low bias voltages [11]. Andersson et al. [12] performed an experiment to examine the morphology and properties of electro less deposition of Ni into p-type PS and the subsequent formation of Ni silicide after heat treatment. They showed that different rectifying and Ohmic contacts can be formed between electro less deposited Ni and PS depending on the heat treatment conditions. Reports [13] are also available on the use of Au, Cu and Ni contact to porous silicon by electro less deposition. Although Au and Cu showed some positive results on oxide formation but Ni was proved to be ineffective.

PS contains a very high density of surface states which arises due to its extremely large effective surface area. So the metal electrode contact to the unmodified surface for the electrical measurements may exhibit an unstable and rectifying behaviour, as the surface states can pin the Fermi level and create barrier against the current flow. It was also verified from our experiments that Al contact to unmodified PS was unstable and rectifying in nature. Therefore to get a stable and reliable electrical contact to PS, the passivation of defect states in the porous silicon is necessary. After passivating the surface states by modifying the PS surface using noble metals, we observed that the Al contact to PS was stable and Ohmic in nature.

In the present investigation a technique was adopted by dispersing noble metals on PS layer by chemical dipping method, followed by brief annealing at low temperature in air. We studied with Pd, Ru and Pt and we observed that Pd shows to be more effective amongst the three perhaps because of the more inclusion

* Corresponding author. Tel./fax: +91 3324146217.
E-mail address: sukumar_basu@yahoo.co.uk (S. Basu).

0038-1101/$ - see front matter © 2009 Published by Elsevier Ltd.
doi:10.1016/j.sse.2009.03.012

of the Pd onto the PS surface which in turn depends on the oxidation reduction potential of the metal [13]. It was also verified from the EDAX line scan analysis. Here we report our results on Pd modification of PS surface. FESEM was done to examine the morphology of the surface. EDAX study and digital X-ray image mapping confirm the dispersion and formation of Pd clusters on the PS surface. From EDAX and XPS results it is verified that the presence of oxygen is higher in modified PS. Al contact to modified porous silicon appears to be low resistive ohmic contrary to the nonlinear nature reported with Al contact on unmodified porous silicon surface [8,14]. The specific contact resistance of Al contact to the modified PS layer was studied using the TLM method. The stability study of such contact is also reported in this paper.

2. Experimental

2.1. Porous silicon formation

On a p-type monocrystalline silicon (100) wafer of resistivity 1–2 Ω cm, porous silicon was formed by anodic etching method in a closed jig [15]. Porous silicon was formed on a circular area of 1.6 cm diameter exposed to the electrolyte. The anodization bath was composed of a mixture of HF (48%) and C_2H_5OH in 7:3 ratios by volume. The back of the sample was coated and fired with aluminium paste for making the anodic contact. A current density of 10 mA/cm^2 for 40 min was applied. The porosity and the thickness of around 55% and 5 μm, respectively. were measured gravimetrically [11,16]. The gravimetric measurements were done using a precision semi microbalance type: 290-9842/K of PAG OERLIKONAG CH-DIETKON (Switzerland).

2.2. Modification of porous silicon surface

PS samples were dipped into 10% HF solution for 10 s to remove the native oxide layer to a large extent and were immediately dipped into aqueous $PdCl_2$ solution (containing 2–3 drops HCl) of different molar concentrations (0.01 M, 0.005 M, and 0.001 M) and for different times (5–180 s). Subsequently, the samples were rinsed gently by DI water and were dried in air followed by annealing in air at 110 °C inside an electric oven for 10 min.

The chemical modification steps are cited as follows:

$$PdCl_2 \rightarrow Pd^{++} + 2Cl^-$$
$$Pd^{++} \rightarrow Pd\ (\text{Island}) + 2h^+$$
$$Si + 2H_2O + 2h^+ \rightarrow Si(OH)_2 + 2H^+$$
$$Si(OH)_2 \rightarrow SiO_2 + 2H^+ + 2e^-$$
$$2H^+ + 2e^- \rightarrow H_2$$
$$2Cl^- + 2H^+ \rightarrow 2HCl$$

Pd^{++} formed by decomposition of $PdCl_2$ in an aqueous acidic solution is reduced to Pd metal islands by a chemical reduction process [13] and two h^+ are released. Subsequently PS surface gets oxidized by h^+ to SiO_2.

Unmodified and modified porous silicon surfaces were characterized by FESEM and EDAX. The distribution of nano sized Pd on the modified porous silicon surface was studied by digital X-ray image mapping. All these characterizations were carried out using the electron microscope JSM-6700 F; JEOL, Inc. XPS was also performed to find out the chemical nature of the modified PS surface. The XPS measurement was performed by a VG microlab Auger/XPS Spectrometer with a 310-F analyzer. The measurements were carried out with Al Kα photons (1486.6 eV) and during the measurements the base pressure was around 2×10^{-8} mbar.

2.3. Formation of electrical contacts to PS surface

Al metal pads of 0.2 μm thickness were deposited over the modified porous silicon surface by thermal vacuum evaporation ($\sim 10^{-5}$ torr) using an appropriate metal mask and was annealed at 450 °C in nitrogen containing 2% hydrogen for 15 min. Thin Cu wire connections were taken to the Al electrodes using silver paste followed by heat treatment at 110 °C for 10 min in air. *J–V* characteristics were studied and TLM method was used to get the specific contact resistance of Al contact to porous silicon. A high precision Keithley meter (Model no. 6487) was used for the electrical measurements. Similarly, Au contacts were made to PS by thermal evaporation ($\sim 10^{-5}$ torr) of Au and thin Cu wires were connected using silver paste for *J–V* measurements.

3. Results and discussions

3.1. Structural characterization

Fig. 1 displays the FESEM images of porous silicon surfaces both unmodified and modified with 0.01 M $PdCl_2$ solutions for 5 s. Images were compared at similar magnifications. It appears from the FESEM that both unmodified and modified PS layers are nano porous by nature and pores are not totally covered with metals.

EDAX of the modified sample confirms the presence of Pd as shown in Fig. 2 and also oxygen is higher in Pd modified PS compared to the unmodified one.

In Fig. 3a the XPS of the unmodified porous silicon surface shows a strong doublet at around 100 eV corresponding to pure silicon and a small doublet at around 103.5 eV, which agrees well with SiO_2. The spectrum of Pd-modified surface, on the other hand,

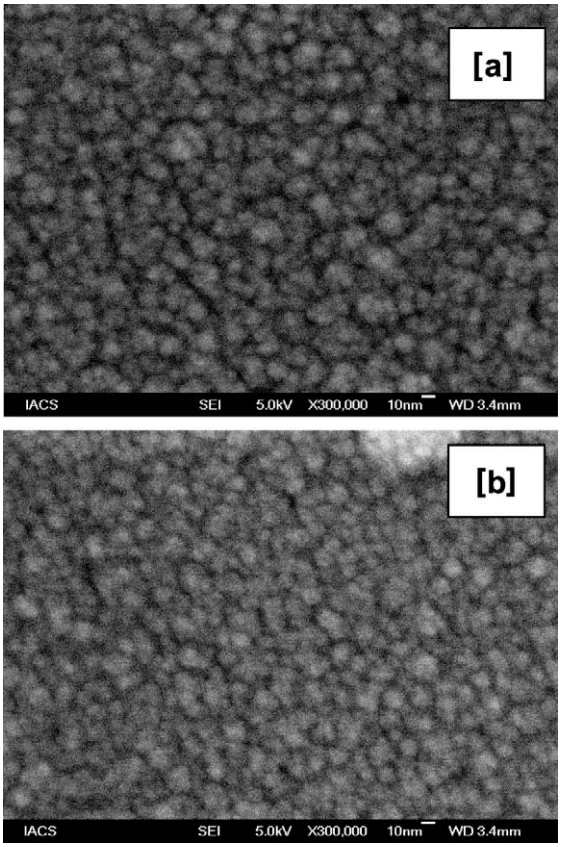

Fig. 1. FESEM of (a) unmodified PS surface and (b) PS surface modified with 0.01 M $PdCl_2$ solution for 5 s.