Copper Displacement Deposition on Nanostructured Porous Silicon

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ABSTRACT

Immersion displacement technique innovated by introducing of hydrofluoric acid in solution for Cu deposition was used to decorate porous silicon with Cu. Porous silicon surface was found to be covered by Cu nanosized crystals. Simultaneously porous silicon skeleton was observed to dissolute during Cu solution immersion step. Principally different nanosized objects from porous silicon covered with separated or coalesced Cu nanoparticles to porous Cu membranes were formed. It was found variation of porous silicon preparation regimes allows creating both the rectifying and the ohmic Cu/porous silicon contacts. Crystallographic orientation of the initial Si and porous silicon porosity were revealed to strongly effect on conductivity of Cu films. Finally free standing porous silicon layer was converted into flexible porous Cu membrane by displacement method. Thickness of Cu membrane reached to 25 μm and its electrical conductivity was equal to 60-70% of bulk Cu.

Keywords: porous silicon, copper, displacement deposition.

1 INTRODUCTION

Despite of its long-standing discovery, porous silicon (PS) has been still attracting great attention in the field of nanoscience and nanotechnology by the present time due to its exeptional properties and potentional applications as breakthrough material for optoelectronics, MEMS, layer transfer technology, solar and fuel sells, etc. [1]. PS is considered as interesting support material for sensory properties because of its extremely high effective surface area, large adsorption capacity, unique optical properties and biocompability. Paper [2] has reported about nanostructured PS covered with Ag nanoparticles as SERS substrates. It is provided by plasmon's appearance in noble metals and Cu films of one to tens nanometers roughness which is usually reached by deposition of mentioned metals on PS. In this regard, numerous studies have been undertaken to modify PS surface with metals to obtain the desired properties suitable for sensor applications [3][4]. Extremely tempting goal is to minimize the complexity and the cost of PS based sensors production. It requires cheap materials, high repeatability and simplification of the technological process by exeption of the operations or their combining. That is why great attention has been directed exactly on immersion displacement deposition (IDD) of copper on PS. Copper is characterized by its redox chemistry, thermal, catalytic and sensing properties as well as low price in comparison with noble metals. Moreover copper has been using as the main material for metallization of ICs since 90th of last century due to its high electrical conductivity. IDD of copper on PS has many advantages such as simple control of deposition, no need in special equipments, penetration of metal atoms in porous layer providing high adhesion of Cu contacts to PS. Peculiarity of such method is the convergence of copper reduction with porous silicon dissolution.

In the present work we have presented different nanosized structures formed by the IDD of Cu on PS. Previous study has given the results of using of copper salt aqueous solutions for porous silicon plating with metal [5]. But the process has been accompanied with silicon oxidation which inhibited copper deposition. It has been proposed to optimize IDD by fluorine ions addition in standart copper salt solution for prevention of PS oxidation which had been taken place in previous studies [6]. It has provided direct contact between Si skeleton and Cu. Moreover Si nanocrystal sizes monitoring by the control of its dissolution during copper deposition significantly expends the collection of nanoscaled structures obtained by the mentioned technique.

2 EXPERIMENTAL DETAILS

2.1 PS Formation

Monocrystalline n^+-type (100) and (111)-oriented Si wafers were used to fabricate PS layers. Wafers were chemically cleaned in standard RCA solutions. PS was formed by an anodization in the Teflon cell with an active area of 3 cm^2. Mixture of HF (45%), H_2O, and C_3H_7OH in a 1:3:1 ratio by volume composed the anodic bath. Current density and time of anodization were varied to provide the necessary properties of PS. After electrochemical etching the samples were cleaned in distilled water and isopropyl alcohol.

2.2 Copper Deposition

Immediately after PS formation cleaning liquid was replaced by 0.025 M $CuSO_4 \cdot 5H_2O$ + 0.005 M HF aqueous solution for different time-periods at room temperature and Cu was deposited onto PS according to the chemical

displacement mechanism. The copper treated PS was cleaned with isopropyl alcohol and finally dried under air stream of 40°C temperature.

2.3 Characterization

Gravimetric method was used for the determination of PS porosity. Anodic current density of 60-120 mA/cm^2 provided fabrication of PS layers of 45-85% porosity.

Scanning electron microscopy (SEM) was used to obtain an information on the experimental samples morphology. The analysis of the top views and cross sections of the pristine and copper treated PS was done by high resolution SEM (Hitachi-S4800). Feret's statistical diameter method was applied to estimate Cu particle size and their distribution on PS surface.

X-ray diffraction (XRD) analysis was performed to determine the structure and crystallographic phases of the samples. Characterization was done by XRD in DRON-3 diffractometer operating with monochromatized CuK_α radiation of wave length 0.154 nm. Before XRD analysis samples were left on the open air during 2 weeks to estimate oxidation stability of copper.

Conductivity of the Cu treated PS samples was measured by 4-probes standard method. Copper probes were set along the line paralleled to the sample surface and contacted with an analyzed surface by the device which provided pressure repeatability. Each experimental sample of 3 cm^2 active area was measured in 15 different points by the described technique to determine data spread.

3 RESULTS AND DISCUSSION

3.1 XRD Analysis of Copper Treated Porous Silicon

The crystallinity of the copper on PS, deposited by IDD, was assessed from their XRD patterns. The XRD patterns of the PS samples of 55% porosity based on (100) Si treated in copper solution during 20 s and 180 s are represented in Fig. 1a and b, respectively. The 20 s treated sample in Fig. 1a shows peaks corresponding to only (111) and (200) copper, whereas the 180 s treated sample in addition shows peaks (see Fig. 1b) for (220) and (311) copper as well. In each case, the peaks of (111) copper have the greatest intensity stacking together in an ascending order. It noticed about copper crystals (111) prevalent growth during deposition. However copper treatment time increasing led to the nucleation and growth of copper crystals of other orientations. The intensity value and crystal orientation of XRD patterns of copper treated PS of 85% porosity were the same to the Fig. 1. So the weigth of the deposited copper is not depended on initial porosity of PS. But there was substantial difference seen in the diffractograms recorded for copper treated PS based on (100) and (111) Si substrates. The (111) Si based samples presented peaks corresponding to copper crystals of lower intensity in comparison with (100) Si as well as Cu_2O crystal peaks. This significant difference in the case of (111) Si based samples in XRD patterns shows lower oxidation stability of copper crystals with respect to Cu deposit on PS based on (100) Si.

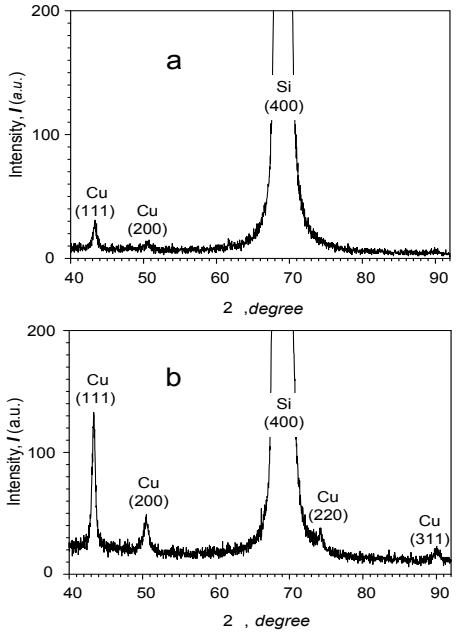


Figure 1: XRD patterns of 20 s (a) and 180 s (b) copper treated PS of 55% initial porosity based on (100) Si.

3.2 SEM Analysis of Copper Treated PS

Series of PS samples were examined by SEM after treatment in different IDD regimes. Fig. 2 shows SEM top views (a, c, e) and the results of Feret's analysis (b, d, f) of 55% porosity PS based on (100) Si, immersed into the solution for (a, b) 20, (c, d) 60 and (e, f) 180 s. Provided SEM images show a non-continuous film consisted of copper NPs with different dimensions over a porous layer. Common view of all Feret's histograms looks like an asymmetric bell which has more long right shoulder. That indicates about grate inequality of distribution, i.e. NPs of the beginning of dimensional range were prevailed. On the other hand large NPs grew at the same time but their number is less. From the very outset of the process copper deposited as separated NPs which diameter ranged from 43 to 197 nm (see Fig. 2 a, b). The real density was 669 NPs per 4.463 μm^2. IDD time increasing led to insignificant size growth of NPs and according to Feret's histogram (Fig. 2 d) their dimensions varied from 45 to 202 nm. Distribution bell body expanded in the area of large NPs and number of counted NPs decreased to 556. Consequently connection of some NPs took place. Further staying of PS in the solution (Fig. 2 e, f) resulted in coalescence of NPs into quasi-continuous copper film. Distribution "bell" has lost left shoulder and maximum of dimensional range shifted seriously to 237 nm as well as density of caught NPs increased to 735 particles per 4.463 μm^2.

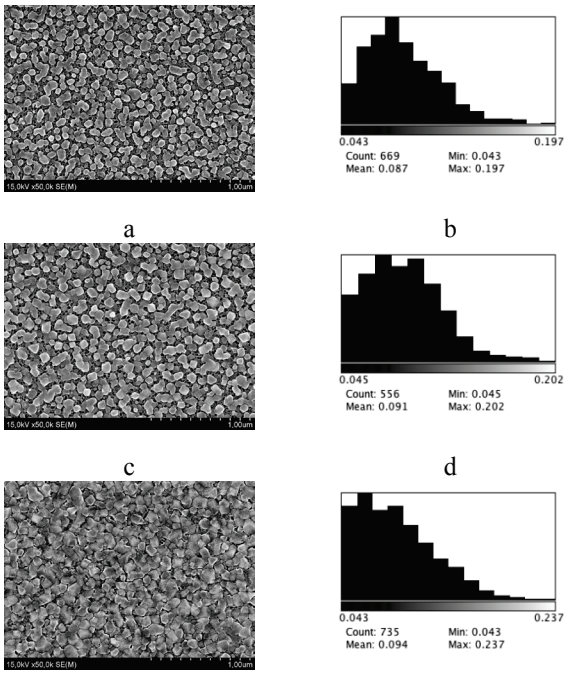


Figure 2: SEM top views and histograms of Feret's analysis of the PS sample immersed in $CuSO_4 \cdot 5H_2O$+HF aqueous solution for (a, b) 20, (c, d) 60 and (e, f) 180 s.

According to the SEM images we divided process of copper deposition in two stages:

1) nucleation and size growth of the primary copper NPs;
2) NPs coalescence into quasi-continuous copper film and nucleation of secondary Cu NPs.

Density of NPs deeply fell between stages of nucleation and fabrication of quasi-continuous film. Such effect is explained in the following way. Initially born NPs grew and some of them coalesced forming bigger particles (Fig. 2 c). Connected NPs are fixed by Feret's analysis as whole one.

SEM images of 85% porosity PS demonstrated no coalescence of Cu crystals into continuous film even after 180 s IDD. The character of copper crystal distribution was not remarkably depended on the orientation of an initial silicon substrate.

3.3 I-V Characteristics of Copper/Porous Silicon Structures

Fig. 3 presents I-V curves for two groups of samples based on (a) (111) and (b) (100)-oriented Si. We varied porosity (P=45, 65, 85%) of PS for each group. The time of copper deposition was 180 s in all cases. We were able to note the following features of analyzed structures. Under forward bias: (a) current exponentially grew with voltage increasing, i.e. contact formed Schottky junction; (b) differential resistance grew with increasing of porosity; (c) differential resistance of structures formed on initial (100) Si was higher than on (111). Under back bias: (a) if U<2V than $I \sim V^a$ (a = 0.5…2), in the other cases I-V curves had linear view; (b) reverse current in the (100) Si based structures was lower than direct current, i.e. rectifying contact was obtained; (c) differential resistance dependence on porosity of structures formed on initial (100) Si was not different from the forward bias case, but samples based on (111) Si showed decreasing of differential resistance with porosity increasing.

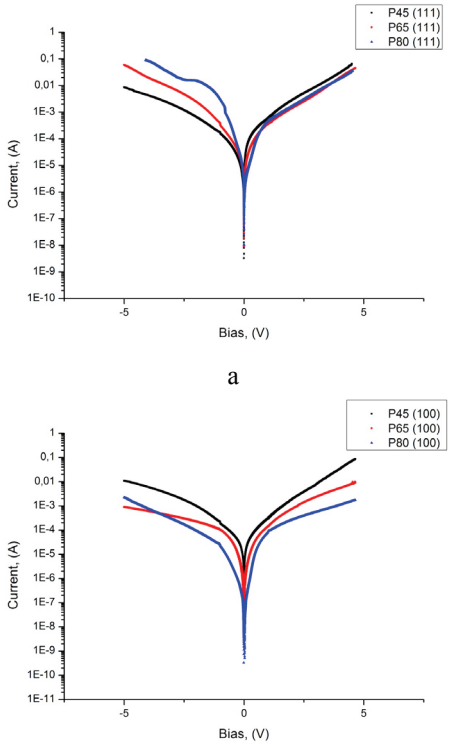


Figure 3: I-V characteristics of Cu/PS structures based on (a) (111) and (b) (100) initial Si substrates.

3.4 Electrical conductivity of Copper Films on Porous Silicon

Electrical conductivity of the outer copper film on PS surface was measured to understand availability of IDD technique for copper interconnect metallization. Fig. 4 shows graphic copper film conductivity dependancies on the time of IDD for different PS samples. All curves have the same character. Conductivity tends to increase with time of IDD prolongation. Samples of (111) and (100) initial Si has insignificant conductivity spread all over the sample active area both 120 s and 180 s copper treated PS. SEM images presented almost continuous films for such times of IDD. In several cases it was impossible to obtain conductivity data due to its great unstability. Copper films formed during the time periods less than 60 s on PS with porosity of 85% were not allowed to estimate their conductivity. According to SEM analysis such films presented the layer of separated copper crystals which

provided difficulties for current leaking. Commonly porosity increasing from 55% to 85% led to conductivity falling. So copper films deposited on PS based on (100) Si showed better conductivity in comparison witn case of PS based on (111) Si. We suggested that such effect may be due to copper oxidation previously mentioned. Copper films on 180 s treated PS based on (100) Si demonstrated the best conductivity result. It was equaled to $1.2 \cdot 10^5$ $Ohm^{-1} \cdot cm^{-1}$ and was only in five times less than conductivity of bulk copper.

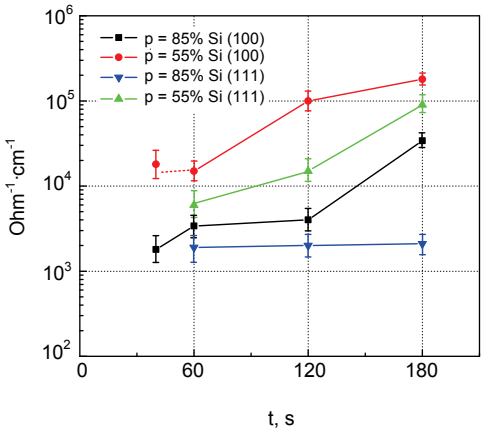
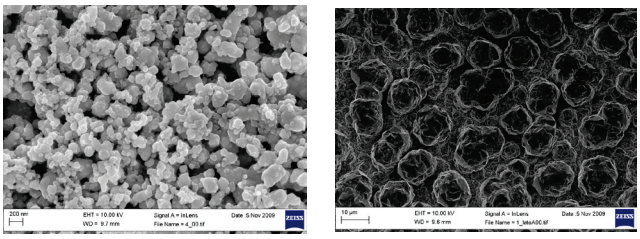


Figure 4: Conductivity of Cu films on PS vs IDD time.

3.5 Porous Copper Membrane

As it was noticed in the paper, introduction optimization of the IDD solution with fluorine ions allows to control dissolution process of Si skeleton of PS. So, we were successful to fully displace Si atoms of PS free membrane by Cu atoms. Fig. 5 shows SEM top (a) and bottom (b) views of Cu porous membrane formed by conversion of free standing porous silicon layer with using IDD method. Membrane presented flexible porous copper layer of 25 μm thickness. Electrical conductivity of porous copper film was 60-70% of bulk copper. Two porous copper membranes were used as electrodes for supercapacitance with liquid electrolyte. Three orders of magnitude increase of capacitance for porous copper electrodes was experimentally measured as compared with flat nonporous electrodes.



a b

Figure 5: SEM top (a) and bottom (b) view images of porous copper membrane.

4 CONCLUSIONS

Principally different structures were obtained by copper IDD on PS. IDD was presented as method for decoration of PS with copper Cu NPs of such dimensional range which according to may be applied in SERS [5] or ellipsometrical [6] sensors production. Successful introduction of mentioned substrates in this direction requires additional study of their sensitivity. It has been found variation of the PS preparation regimes allows creating both the rectifying and the Ohmic Cu contacts to PS. Copper films deposited on 55% porosity PS based on (100) Si showed good electrical conductivity for Cu metallization application. In addition, IDD was demonstrated to be used for porous copper membranes fabrication.

ACKNOWLEDGEMENTS

This work was supported by the grant № T10M-089 from the Belarusian Republican Foundation for Fundamental Research. Authors would like also to thank Vitaly Bondarenko for helpful discussions, Vladimir Tsubulskii for SEM images and Kazimir Yanushkevich for X-ray diffractometry.

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