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EFFECT OF FORMATION OF BILATERAL POROUS STRUCTURE IN ETCHING PROCESS OF SILICON PLATES DOPED BY AN ARSENIUM

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The article is dedicated to the research of physical processes occurring on the cathodic side of porous silicon. Porous silicon is formed by Unno-Imai electrochemical method. The essence of electrochemical method Unno-Imai consists that at direct current transiting through an electrolyte, on an anode effective area porous silicon is shaped. The presence of the modified porous layer was discovered on the cathodic part. The structural analysis proved that this modified layer conserves its monocrystalline silicon base. Results of investigations have allowed praposing the hypothesis that modified layer has porous structure.

Introduction.

Porous Silicon (PS) was discovered in late 50's of 20th century as an outcome of electrochemical tanning operation [1, 2]. The application perspectives of PS require to compile its electrophysical parameters,its stabilization methods for radiation tolerance and information about options of PS-Metal and PS-Si transitions.

One of widespread forming methods of PS structures is Unno-Imai [1] method. Fabrication of porous structure with this method in a considerable quantity has allowed detecting the new phenomenon that has not been found by anybody earlier.

In the works devoted to electrochemical processes by method Unno-Imai with a direct current [8,9], it was specified that the cathodic part of a silicon plate is inert and much of physical processes happen in anodic part. Yet, cathodic part does not show any sign of practically and scientifically beneficial processes [8]. However, our experiments showed that such statement is not always correct and under certain conditions, there are essential changes in subsurface layer of silicon in a cathodic regime. Such changes were observed on the cathodic part of strongly doped plates $p^+ - Si$, $n^+ - Si$ and they were shown particularly bright on plates with electronic type of conductivity.

The main objective of this paper is to investigate physical processes happening on the cathodic part of porous silicon during the process forming porous silicon with the help of Unno-Imai and to conclude with results of experiments.

Experimental measurements.

Plates with 10-40% porosity (111) [1] were anodized within normal conditions on the HF base-electrolyte (46 % water solution HF, 46 % water solution HF + isopropanole) at anodizing current density of $5 \div 40\, mA/cm^2$ during $10 \div 60$ minutes with an $320\,lk$ illumination. Illumination was designed such that it could expose both cathode and anode platesides. In this case traditional PS structure with thickness $20 \div 160\,mcm$ on the working (anode) side and thin modified layer of silicon on cathode side appeared. The thickness of this layer reaches to $2 \div 8\, mcm$ at the high density of a current during long-term fabrication process of $n^+ - Si$ plates. That modified layer's photo on electronic microscope shown on Fig. 1, as well as on optical microscope on Fig. 2 . Crystal structure of the modified layer has been executed on x-ray diffractometer ДРОН -2 by radiation of a cobalt source. The new phases were not revealed on roentgenogram and the reflexes corresponding to orientation (111) of silicon have been recorded. It turns out that the modified layer keeps its monocrystalline base.

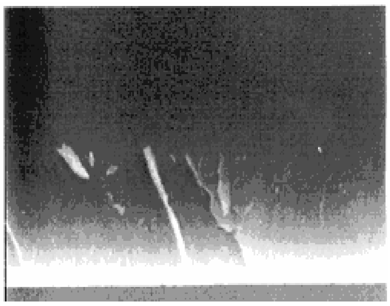

Fig. 1. Raster-type electronic microscope (REM) the image of the modified stratum on the cathodic leg of plate КЭС-0,01 of orientation (111).

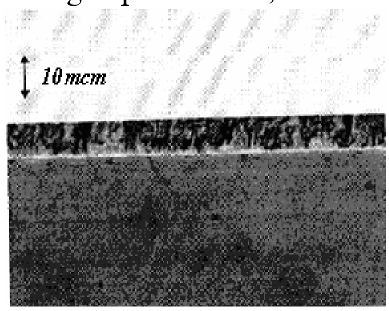

Fig. 2. Optical picture of a thick modified stratum on the cathodic leg of a plate of n-type of conductance.

The Chemical composition of layer in cathodic part of plate has been identified by -spectrometer PHI-660 and mass spectrometer CAMECA IMS4F.Results of profile measurements of a various elements showed that a silicon is dispersed equally over all thickness of the modified layer and it even does not change in case of penetrating through the depth of silicon plate (Fig.3) . The modified layer has indicated to possess the enriched oxygen and carbon distributed equally over the surface of a layer. Existence of considerable quantity of atoms of platinum and rhodium in the volume of a layer studied is a characteristic case. (The elements that are a part of an electrode. If such atoms would make 3 % nuclear percent on the surface, this percent will decrease while approaching the surface).

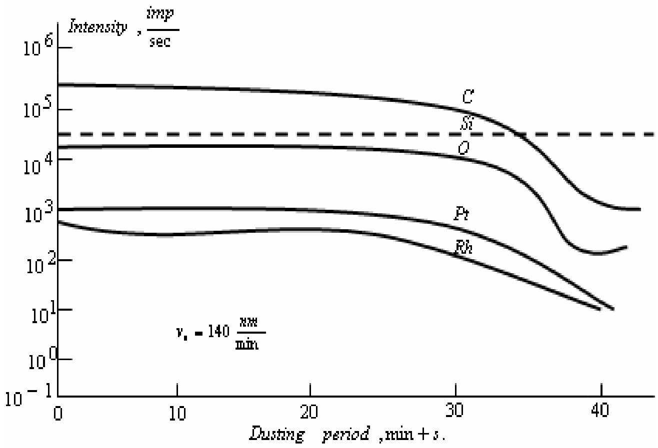

Fig. 3. Lateral view of allocation of chemical elements in volume of the modified stratum according to Mass spectroscopy. The pulverisation was manufactured by a bundle of ions of an argon.

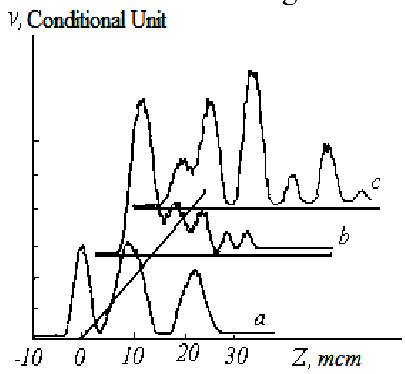

Fig.4 . V (z)-curve Surface Waves of Rayleigh for initial silicon КЭС-0,01 (a), for PC on the anodic leg (в), the modified stratum on the cathodic leg (c).

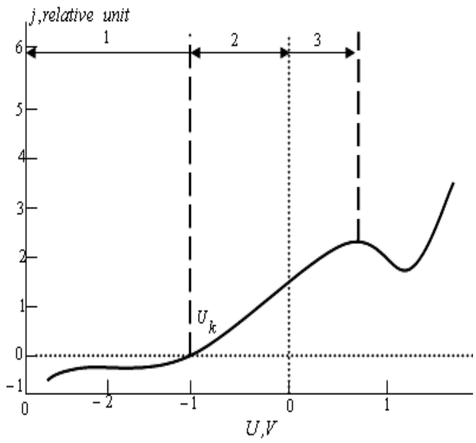

Fig.5 Typical view of volt-ampere characteristic of contact p-Si/HF [6]. Fields: 1 - hydrogen allocation, 2 - PC shaping, 3 - an electropolish.

Results and Discussion.

It should be noted that there are no electrode metals in the components of porous material on plate's anode part. Results of the given researches have allowed advocating an assumption on porous structure possession of the modified layer:

1) Layer preserves monocrystalline structure that is characteristic for porous silicon with low porosity.

2) The quantity of oxygen and carbon in the modified layer, and a profile of distribution of these elements have appeared practically the same as profile of quantity of porous silicon on the anode part of a plate. During electrochemical processing, the penetration of ions Pt and Rh into depth of silicon for several microns is related to strong development of pore matrix.

The measurement session of V(z) -curves Surface Waves of Rayleigh on acoustic microscope ELSAM was held in order to learn structure of the modified layer.

Curves of V(z) drawn at radiation frequency $3 \cdot 10^9\ Hs$ for original silicon, porous anode part of silicon and the modified layer on the same structure are shown on Fig. 4. Speed of the surface waves in silicon equals $4780\ m/s$. Surface Waves speed on a porous layer of the anode part equals $3200\ m/s$, which is compatible with 40 % porosity of the MS structure. Surface Speed of wave on modified layer is $3900\ \mathrm{m/s}$. Such value of speed reveals the existence of structure with 22% porosity. Thus, modified structure on cathode part of plate has different characteristics. Forming process of a porous layer on the cathode segment of a plate, along with formation of a layer of the PS structure on the anode part, can be explained as follows. It has been shown in the works dedicated to processes poreregeneration on boundary of silicon/HF for n - and p-type silicon plates (Fig.5) that poreregeneration is possible not only in an anode regime, but also in a cathode regime at small $|U| < |U_k|$ displaycement. U_k can be equal to several hundreds of mV .Quantity U_k can make some hundreds mv. In a method of fluid contact Unno-Imai voltage U given on electrodes, is proportioned between all devices of an electrolytic cell

$$U = U_1 + U_2 + U_3 + U_4 + U_5 .$$

Where U_1, U_2, U_3, U_4, U_5 - a voltage drop on the left volume an electrolyte, on contact an electrolyte / the anodic leg, on a silicon plate, on contact an electrolyte / the cathodic leg and on the right volume of an electrolyte, accordingly. Quantities of these components will depend on relations of electrical resistances of each device (concentration HF, level of a doping of silicon etc.). It is necessary to score, that for strongly alloyed plates of silicon the material resistivity comparable or is less than electrolyte resistivity. On a site an electrolyte / the cathodic legat certain parametres can obey given negative voltage U_4 cavitation process $|U_4| < |U_k|$ but for realisation of growth of pores it is necessary to have in addition performance of one more equirement: the amount of electron defects on the cathodic leg of a plate should be sufficient for a cavitation.

However, it is important to meet one more requirement in order to implement poreregenaration: the of plate must number of holes in cathode part of plate must be enough for poreregenaration. This can be done

1) By extra illumination of cathode part of plate. Since field intensities are small on lowohmed silicon plates, drift of holes to anode part goes slowly. In this case a photogeneration of holes on the cathode part of the plate can be sufficient requirement for poreregeneration.

2) The effective delivery of holes to the cathodic part of a plate can be realized by means of the following mechanism. It is known that intensive allocation of hydrogen occurs on the cathode part of a plate [4,5].

It is known that during electrochemical processes intensive discharge of hydrogen happens on cathodic part of the plate [2, 6]. The hydrogen discharge occurs because electrochemical reload:

$$2H^{+} \rightarrow H_{2} + 2h^{+}. \tag{1}$$

Where, h^{+} - plus electron defects. Consequently, a drift of hydrogen ions under the influence of electric field in the right volume of electrolyte to the cathode part of a plate and passage of reaction (1) creates the additional holes necessary for realization of poreregeneration process.

As stated, a formation of a porous layer on the cathode part of $n^{+}-Si$ plates occurs more intensified compared to that of $p^{+}-Si$ plates. In this case, the thickness of the modified layer can reach to $6 \div 9$ mcm for $n^{+}-Si$ plates while for plates $p^{+}-Si$ the thickness of the modified layer seldom exceeds 1 mcm . This is explained by the fact of transition of electrolyte / the cathode part for n -type plates processes in a direct direction [6, 7], and for p-type plates - in the back. Modified layer forming on the cathode part of silicon plates with hole type of conductivity possesses one more feature. It has been found that modified layer partially collapses at the high density of a current and during the long-term anode processing of $p^{+}-Si$ plate. This phenomenon reveals itself structure particle on electronic microscope and as erosion cavities on the surface of the modified layer (fig.6, fig.7). Non-existence of the modified layer on poorly alloyed silicon plates can be explained with negative displacement of U_{k} being considerably slight or completely absent which is important condition for poreregeneration [3, 9].

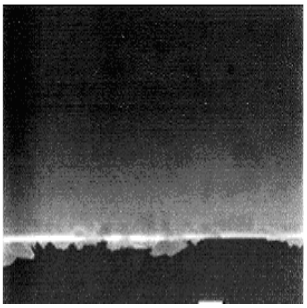

Fig. 6. Fracture of the modified stratum on silicon substrates(substructures) of p-type of conductance at major times of the treatment(processing), observed on skole structures.

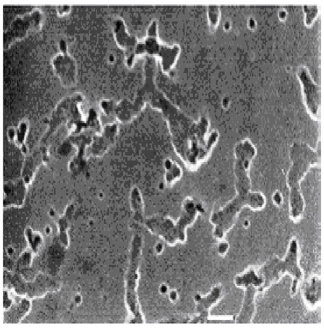

Fig. 7. The REM-IMAGE of a surface of the modified stratum given on fig.2 .

Thus, the results of the spent researches carried out show possibility of generation of the second porous layer on the cathode part of the highly doped silicon plates with Unno-Imai method on a direct current. The necessity of creation thermoisolating (heat-shield) layers in silicon structures has enhanced attention substantially toward forming processes of two-layer porous structures. The modified layer forming on the cathodic part of plate is the compilation of porous structures with different structures. In order to achieve this either polarity of delivered voltage changes or it is anodized with impulses having different polarity in Unno-Imai method.

Modified layer possesses enriched oxygen and carbon scattered over the surface. Research has also determined the presence of platinum and rhodium atoms in modified layer.

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ARSENLƏ LEGİRƏ OLUNMUŞ SİLİSİUM LÖVHƏLƏRİ SƏTHİNDƏ İKİTƏRƏFLİ MƏSAMƏLİ STRUKTURUN YARANMASI EFFEKTİ

H.Ə.HƏSƏNOV, R.Ş.RƏHİMOV

XÜLASƏ

Məqalə arsenlə qegirə olunmuş silisium səthində məsaməli silisiumun elektrokimyəvi Unno-İmayi metodu ilə formalaşdırılması prosesində lövhənin katod tərəfində baş verən fiziki hadisələrin tədqiqinə həsr olunmuşdur. Elektrokimyəvi aşılama prosesində lövhənin katod tərəfindəki səthində modifikasiya olunmuş təbəqə aşkar olunmuşdur. Struktur təhlili göstərir ki, modifikasiya olunmuş təbəqə monokristallik silisium bazisin strukturunu saxlayır. Tədqiqatların nətijəsi modifikasiya olunmuş təbəqənin məsaməli struktura malik olması mülahizəsini irəli sürməyə imkan verir.

ЭФФЕКТ ФОРМИРОВАНИЯ ДВУХСТОРОННЕЙ ПОРИСТОЙ СТРУКТУРЫ В ПЛАСТИНАХ КРЕМНИЯ, ЛЕГИРОВАННЫХ МЫШЬЯКОМ

Г.А.ГАСАНОВ, Р.Ш.РАГИМОВ

РЕЗЮМЕ

Работа посвящена изучению физических процессов, происходящих на катодной стороне пластины кремния, легированного мышьяком при формировании пористого кремния электрохимическим методом Унно-Имаи. Обнаружено наличие модифицированного слоя на катодной стороне пластины. Структурный анализ показал, что модифицированный слой сохраняет структуру монокристаллической кремниевой основы. Результаты исследований позволили высказать предположение о пористой структуре модифицированного слоя.