‘Device structures on porous silicon studied by scanning electron microscopy in the electron-beam current mode

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Contacts metal/porous silicon and p/n device structures on porous silicon were studied by scanning electron microscopy in the electron-beam-induced current mode. It is shown that the drift processes are dominant in operation of porous silicon-based devices. We present the theoretical analysis of electron-beam-induced current measurements and estimate such important parameters of device structures as: the width of the space-charge region (several microns), charge state density in the space-charge region \(10^{14}–10^{15} \text{cm}^{-3}\), and electron drift length (up to \(10^{-3} \text{cm}\)). The spatial distribution of the electric field in space-charge region was derived. The possibility of studying the influence of porous silicon/crystalline silicon interfaces on operation of porous silicon-based devices has been illustrated. © 1996 American Institute of Physics. [S0021-8979(96)00413-6]

I. INTRODUCTION

Porous silicon (PS) draws attention from various research groups due to its potential application in optoelectronics. This interest is stimulated by a strong visible light photoluminescence (PL) from PS.1,2 Presently, light-emitting Schottky barrier,3,4 homo5 and hetero p-n junction devices,6,7 photodetectors,8 and solar cells9 based on PS have been demonstrated. However, the parameters of such devices are not all that impressive and, in particular, the quantum efficiency of electroluminescence10 does not exceed \(10^{-4}\). The reasons for such poor performance are not quite clear mainly because the underlying physics of operation of PS-based devices is not well understood.

As a rule, PS-based devices contain two potential barriers: one at a PS/c-Si heterojunction, and another at a metal/PS junction or a p-n junction. The impact of each of these junctions on device performance has not been extensively studied. It has been shown that the current–voltage characteristics of Me/PS/c-Si structures for low forward biases are governed by the PS/c-Si potential barrier.11 For reverse bias such information is lacking. For p-n structures these studies have not been reported. There is practically no information on the barrier’s parameters, such as the width of space-charge region (SCR), electrostatic potential distribution, density of charge centers in SCR, etc. The relative contributions of diffusion and drift processes in charge transfer and resulting photocurrent of PS devices have also not been evaluated.

In this work we report, for the first time to our knowledge, the results of scanning electron microscope (SEM) measurements of PS structures using an electron-beam-induced current (EBIC) regime. It is shown that such measurements could be very efficient in elucidating the nature of the processes determining the transport of nonequilibrium charge carriers. We present the results of our studies of Schottky barriers, p-n junctions, and PS/c-Si interfaces.

II. EXPERIMENT

PS layers of 3–30 \(\mu\text{m}\) thickness were prepared by electrochemical etching of c-Si in HF-ethanol solution (1:2). Anodization was performed in a Teflon anodization cell with a Pt mesh as the cathode. The Si electrode was mounted horizontally. The polished face of the wafer was exposed to the electrolyte, and its backside with the ohmic contact was pressed to a Cu plate. The surface area exposed to the electrolyte was 2 cm\(^2\). Before mounting, wafers were surface treated in boiling toluene for 5 min, in a mixture of HNO\(_3\):HCl=1:1 for 5 min, and subsequently well rinsed in de-ionized water. The back ohmic contact was prepared by vacuum deposition of Al and subsequent annealing at 550 °C. Anodization was performed under galvanostatic regime. The anodic current density was 20–90 mA/cm\(^2\), the etching time was 5–15 min. The peak of the PL spectra of these PS layers corresponded to 0.67–0.75 \(\mu\text{m}\).

For Schottky diodes preparation, p-Si (111)-oriented wafers with resistivity about 10 \(\Omega\) cm were used. Au or Al dots of about 1.2 mm in diameter were deposited in high vacuum through a shadow mask. For p-n junction preparation, c-Si samples with an \(n^+\)/p junction were used as a substrate. The \(n^+\)/p junction was prepared by phosphorus diffusion into p-type silicon wafers with resistivity of 3–5 \(\Omega\) cm. The junction depth was 1–3.5 \(\mu\text{m}\) as determined by the peak in EBIC current. PS layers were prepared from the \(n^+\) side.

EBIC measurements were made on the cleaved samples using a JSM-U3 SEM. Accelerating voltages were 25–38 kV, the primary electron current was about \(10^{-10}\) A, and the electron probe diameter on the sample surface was about 0.1 \(\mu\text{m}\).

III. RESULTS

SEM measurements in the secondary electron (SE) mode on the cleaved samples allowed establishment of the thickness of the PS layer and the position of the PS/c-Si interface.
In most cases this interface is revealed as a region with higher SE yield. For some samples the SE yield for the PS layer and the substrate was also different (see Fig. 3 below).

In Fig. 1 we present line scans of the EBIC current ($J$) for cleaved unbiased Me/PS/c-Si structures. The presence of a characteristic maximum in $J$ near the PS/c-Si interface indicated that electron-hole pairs are separated at this interface. At the same time, in contrast to Ref. 11 where generation was done by laser beam and no Schottky-barrier-related $J$ peak was detected, we could clearly see a maximum in EBIC profile near the PS surface. The relative efficiency of charge collection on both junctions was different for different samples, but the direction of electric fields always coincided for both barriers. In some cases the collection efficiency and $J$ values varied for various regions of the PS/c-Si interface even for the same sample. For some specimens we observed a local minimum in the EBIC signal [Fig. 1(b)] which might be related to a decrease in absorbed electron current due to the enhanced yield of the secondary electrons.

Near the Me/PS interface the $J$ value slowly decreases with the distance from the surface ($x$) [Fig. 1(a)], i.e., the $J(x)$ dependence has the lowest slope near the surface and this slope increases with the increase of $x$. At the PS/c-Si interface we observe an asymmetric peak in $J$ profile.

In Fig. 2 we present the EBIC line scans across the Me/PS/c-Si structures for biases of $U = 0$ and $U = -1$ V. It can be seen that upon application of reverse bias the potential is redistributed between the junctions in such a way as to enhance the influence of the PS/c-Si interface.

Line scan of SE emission (1) and EBIC (2) for the samples prepared by etching the $p$-$n$ junction containing substrates which led to formation of the PS layer with the thickness 12 $\mu$m are displayed in Fig. 3. Abrupt changes in the SE yield correspond to the sample surface and the PS/c-Si interface. In $J$ line scan we observe two peaks: one immediately near the PS/c-Si heterojunction (as for the
Schottky diodes above) and another near the external surface of the PS layer. The $I-V$ characteristics indicate a rectifying behavior of these samples. The forward to reverse current ratio was about $10^4$ at 2 V, and the ideality factor was about 5.

In contrast to the Me/PS/c-Si structures the $J(x)$ profile for the n-PS/p-PS/c-Si structures displays a characteristic feature: near the surface the slope in $J(x)$ is the largest and it decreases as the $x$ value increases. The $J$ peak at the PS/c-Si interface is asymmetric and qualitatively does not differ from the similar peak in Me/PS/c-Si structures. At the same time, for all samples studied the directions of electric fields of the PS/c-Si heterojunction and the $p-n$ junction coincided. The charge collection efficiency of the $p/n$ structures increased with decreasing of the PS layer thickness and reached about 85% for $\sim 3$-$\mu$m-thick layers.

Steiner et al. obtained a $p-n$ junction in their PS layers in the same way as in our article. They used heavily doped $n^+/p^+$ structures prepared by ion implantation of $B$ and $P$ as the substrates.

Some of the samples were prepared in a two-stage process. On the first stage of the etching (10 min) the anodic current density was kept constant at 22 mA/cm$^2$. After that the current density was decreased by 4.5 mA/cm$^2$ each minute during 5 min. Since the crystallite size of $p$-type PS increases with current density decreasing, the structure and $E_g$ of such layers should gradually change along the depth. Hence, for the PS/c-Si interface in this case one should expect the lowest band bending and $J$. This is confirmed by experiment. SE emission and $J$ line scans are shown in Fig. 4 for the direction along the cleaved surface of such sample. It can be seen that the $J$ peak near the heterointerface is practically absent. Hence, the experiment has shown that by changing the growth conditions of PS one can controllably change the magnitude and spatial extension of the built-in field in the heterojunction PS/c-Si.

IV. DISCUSSION

EBIC measurements indicate that the charge collection region in PS-based devices is quite considerable and amounts to several microns. This is in good agreement with the result of Ref. 11 where a peak in light induced current at the PS/c-Si boundary was found to extend to a considerable depth $z$. The large $z$ value was explained in Ref. 11 by the prevalence of light scattering or generation of nonequilibrium carriers in the c-Si substrate due to photoluminescence in PS. It seems to us, however, both processes are not of major importance since otherwise the peak in $J$ in n-PS/p-PS/c-Si structures wouldn’t have been observed near the surface (Fig. 3).

Such extended charge collection regions, $z$, seem, indeed, quite unexpected since one would not anticipate to observe high diffusion length values, $L_d$, in PS. As is very well known, it is the $L_d$ that determines to a large extent the charge collection depth in c-Si. In contrast to the c-Si case, one should assume that in PS the drift processes, and not diffusion, play the main role. This assumption is based in particular on EBIC behavior with changing biases (Fig. 2). Below we present the theoretical analysis of EBIC measurements assuming that the drift processes are prevalent. We will show that the trends observed in the experimental (the maximum in $J$ near the surface of n-PS/p-PS/c-Si structures and some other features) are well explained by this model.

Theoretical analysis of EBIC measurements has been done by many authors. Most of the theoretical treatments refer to the case of high values of $L_d$ and drift length $L_{dr}=\mu E$ (where $\mu$ is the carrier mobility, $\tau$ is the carrier lifetime, $E$ is the electric field strength). In Ref. 14 a particular case for relatively low $L_{dr}$ has been analyzed for a configuration when the scanning probe direction is at right angle to the $p-n$ junction. When the scanning probe is parallel to the $p-n$ junction plane some special cases have been treated, for example, the case when the built-in electric field is absent and the electric field in the sample is created by an external source.

Consider a semiconductor including the barrier with a built-in electric field $E(x)$. This barrier is at right angle to the scanning probe direction. Assuming that generation occurs in infinitely narrow strip near $x_0$ one can write the continuity equation as

\[
\frac{dj_n}{dx} = -\frac{\Delta n}{\tau_e(x)} + j_0 \delta(x-x_0),
\]

where $\delta(x)$ is the delta function, $j_n$ is the drift current density equal to $\mu_n E$; $\mu_n$ is the electron mobility, $\Delta n$ is electron nonequilibrium density minus the equilibrium density, $\tau_e(x)$ is the electron lifetime, $j_0$ is the current density generated at the $x_0$ point. Assuming that $E(x)$ does not depend on generation level we can transform (1), for the region $x<x_0$, where the generated carriers are driven by the field $E$,


\[
\frac{-\mu_n \times E \times d\Delta n}{dx} - \frac{\Delta n \times d(\mu_n \times E)}{dx} + \frac{\Delta n}{\tau_n} = 0, \quad (2)
\]

\[
\mu_n \times E \times \Delta n \big|_{x-x_0} = j_0.
\]

From this one can get for \( \Delta n(x) \)

\[
\Delta n(x) = \frac{j_0}{\mu_n(x) \times E(x)} \times \exp \left( - \int_{x_0}^{x} \frac{dx'}{\tau_n(x') \times \mu_n(x') \times E(x')} \right).
\]

Analysis of the experimental data shows that the surface recombination and the hole current near the surface \((x = 0)\) can be neglected. Otherwise it would have led to compensation of the electron current and to a decrease of the total current when the carriers are generated near this interface. So the current in the external circuit, \( J \), will be equal to

\[
J = q \times \Delta n(0) \times \mu_n(0) \times E(0)
= q \times j_0 \times \exp \left( - \int_{x_0}^{x_0} \frac{dx'}{\tau_n(x') \times \mu_n(x') \times E(x')} \right).
\]

It is more convenient to use the derivative when analyzing the experimental data

\[
\frac{d \ln J}{dx_0} = - \frac{1}{\tau_n(x_0) \times \mu_n(x_0) \times E(x_0)}.
\]

In what follows we will assume that the spatial dependences of \( \mu(x) \) and \( \tau(x) \) are weak. For example, Klima et al. have demonstrated that a substantial dependence of \( \mu \times \tau \) on \( E \) appears at electric field in extent of \((2–4) \times 10^4 \) V cm\(^{-1}\), i.e., much higher than in our experiments \((\sim 10^3) \) V cm\(^{-1}\) (see below).

In Fig. 5 we present the dependences \( dx/d \ln J \) obtained for the Me/PS/c-Si and \( n \)-PS/p-PS/c-Si structures after smoothing the experimental curves in Figs. 1(a) and 3, respectively. It should be noted, however, that by changing the smoothing procedure for \( J(x) \) one can get some scatter in \( dx/d \ln J \) values. Nevertheless, the nature of the \( x \) dependence is not altered, whatever the smoothing procedure.

From the data in Fig. 5, one can see that for the Me/PS/c-Si structures the electric-field strength is at its maximum near the surface and decreases when one moves inward. For the \( n \)-PS/p-PS/c-Si structures the electric field first increases, reaches a maximum at \( x \approx 2.7 \) \( \mu \)m, and then decreases. The position of the maximum apparently corresponds to the \( p-n \) junction location which turns out to be close to the one in the initial substrate (3 \( \mu \)m) before the PS layer formation.

Consider now the \( dx/d \ln J \) dependencies for Me/PS/c-Si in more detail. By integrating the experimental dependence \( dx/d \ln J \) (curve 1 in Fig. 5) one easily gets \( \mu \times \tau \) assuming that it does not depend on \( x \). Indeed, if

\[
f(dx/d \ln J) \times J \times dx = \int \tau_n \times \mu_n \times E(x) \times dx = \tau_n \times \mu_n \times U_{k},
\]

where \( U_{k} \) is the potential barrier height at the Me/PS contact. Setting \( U_{k} \) at about 0.5 V \( \text{meV} \) we get an estimate of \( \mu \times \tau \) as approximately \( 10^{-6} \) cm\(^2\) V\(^{-1}\). The \( \mu \times \tau \) deduced by different methods may vary considerably, in particular because of the difference in the sample properties (density of trapping and recombination centers, the Fermi level position, \( E_f \), etc.) and also due to the differences inherent in the applied methods (i.e., generation level, electric field strength, etc.). The substantial difference between our values and those of TOF could be explained by the fact that the measurements refer to different types of charge carriers (holes in the TOF methods). But the difference between our data and the data of Klima et al. is very substantial and the reason for it is not yet clear.

From Fig. 5 it was deduced in addition the mean electric-field strength in region A (curve 1 in Fig. 5). It is about \( 10^3 \) V cm\(^{-1}\) to which the drift length of \( L_d \sim 10^{-3} \) cm should correspond. From the slope of the \( dx/d \ln J \) dependence one can also estimate the charge density \( \rho \) in the SCR of the Me/PS contact using the relation \( dE/dx = \rho e \). For the A and B regions (curve 1 in Fig. 5) the \( \rho \) value is, respectively, \( 10^{13} \) and \( 5 \times 10^{13} \) cm\(^{-3}\). These values seem somewhat low if one recalls that the PS layers have been prepared on a B-doped substrate with a hole concentration of about \( 10^{15} \) cm\(^{-3}\). However, two factors should be taken into account. First, the porosity of the studied samples is about 80%–90%, hence the total boron atom concentration should be on the order of \( 10^{14} \) cm\(^{-3}\). At the same time, the PS layers contain other charge centers, deep traps related to the Si dangling bonds being the most prominent. As a rule, their concentration is from \( <10^{14} \) to \( 10^{16} \) cm\(^{-3}\) (Refs. 17 and 18). One should also note that for \( U_{k} \geq |E_f - E_{b}| \), where \( E_{b} \) is a middle of the band gap, the density of charge in SCR is determined not by all states but only by the states falling into the energy interval between the \( E_f \) and \( E_{b} \) (Ref. 19). We know also that
$E_f - E_v$ in our samples is about 0.7–0.8 eV$^{12}$ and $|E_f - E_i|$ can be ~0.1–0.2 eV. Hence, the overall density of charge states in SCR of our sample seems to be in the reasonable range of $10^{14}$–$10^{15}$ cm$^{-3}$.

V. CONCLUSION

The results described above show that, by using EBIC-SEM measurements, one can get some important information on electric-field distribution and charge density in the space-charge region of various PS-based device structures and also on mechanisms of nonequilibrium charge transport. We have also shown that the drift processes are dominant in the operation of PS-based devices. We have made estimates of the drift length, of the product of mobility and lifetime, and of the charge density in the space-charge region of the Me/PS contact. The spatial distribution of the electric field in SCR has been derived. The possibility of studying the influence of various potential barriers on operation PS devices has been illustrated. Of course the conclusions about the drift length, electric field profile within the space-charge region, etc., were obtained in the present work under the assumption that the generation zone of nonequilibrium charge carriers is narrow. We are planning to attempt measuring the width of this zone under excitation by an electron beam in the nearest future.