Potential, Temperature and Doping dependence for macropore formation on n-Si with backside-illumination

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Abstract

Applying an anodic bias on a silicon HF contact and illuminating the backside of a n-type silicon wafer allows to create macropores. The formation of "random macropores" is studied in this paper by determination of the influences of the potential, the temperature and the doping level. A statistical approach is used to evaluate the micrographs. The formation of the macroporous layer consists of two phases. Beginning with a plane surface and homogeneous dissolution of silicon, first pores occur after some time . In this nucleation phase the thickness of the homogeneously dissolved Si depends strongly on the doping level and the temperature but only weakly on the applied bias. In a second phase of stable pore growth the density of pores is investigated as a function of temperature and anodic potential. For low doped material we find a strong stabilisation influence of the deep space charge region (SCR) in the nucleation as well as in the stable pore growth phase. Thus an increased anodic bias decreases the density of pores. For highly doped silicon no stabilisation influence of the SCR is found. The pore growth is dominated by the electrochemical dissolution rate, i.e. increasing the potential increases the density of the macropores.

keywords macropore formation, illumination, temperature dependenc, anodic potential, doping dependence

1 Introduction

Applying an anodic bias on a silicon HF contact allows to create pores which differ radically in size, morphology and physical properties depending on the experimental setup [1, 2]. In this paper we discuss the formation of macropores in n-type silicon with backside illumination [1, 2, 3, 4]. By changing the light intensity the generation rate of minority carriers within the silicon and in consequence the etching current may be controlled independently of the anodic potential. In contrast to porouse silicon layers (PSL) the macropores diameters are in the micrometer scale. Using a standard photolithography for generating etch pits as nucleation centers for pore growth, a very regular array of pores can be generated, which serves as a starting point for a Si- microstructuring technique [5] or to create a "photonic crystal" [6]. This paper investigates the dependence on the anodic potential, electrolyte temperature and doping for the macropore formation of "random pores", i.e. we do not prestructure etch pits as nucleation centers for the pore growth.

2 Experimental Setup

Two series of experiments were performed on n-Si (100) with 4 doping concentrations (0.5 Ωcm, 2 Ωcm, 5 Ωcm and 20 Ωcm): The first series at constant anodic bias U_{an}, varying the electrolyte temperature between T = 5°C and T = 30°C and the second with fixed temperature T = 20°C, varying the anodic potential between U_{an} = 1 V and U_{an} = 6 V. Taking a 4 w% HF-solution, the silicon was etched with a current density j = 5 mA/cm^2. SEM analysis was used to yield the information on the pore lengths, pore diameters and distances between the pores.

3 Results and Discussion

Analyzing the growth of random pores, one must distinguish between the nucleation phase and the phase of stable pore growth. Starting from a plane surface, first a roughening of the surface occurs, followed by formation of shallow pores, often with a higher density than the pores in the stable phase, i.e. a number of these pores vanish before stable growth conditions are obtained. Both, the nucleation and the phase of stable pore growth differ strongly for highly doped (0.5 Ωcm) and low doped (20 Ωcm) material.

For investigation of the nucleation phase the thickness d_h (measured with the profile meter DEKTAK 8000) of a homogeneously dissolved Si layer is plotted in Fig. 1 as a function of time. When the thickness d_h reaches its plateau value the nucleation of pores is completed. For highly doped silicon the stable pore growth condition occurs long before the low doped silicon reaches a plateau value, so the duration of the nucleation phase decreases strongly with doping. Since both curves start with nearly the same slope, the mechanism for the *homogeneous* anodic dissolution of silicon seems to be almost independent of the doping. The thickness d_h does not depend strongly on the applied potential as pointed out in Fig. 2 for different doping concentrations. As shown in Fig. 3 the thickness d_h decreases as a function of the electrolyte temperature. The mayor effect of the applied potential is to increase the thickness of the SCR. The enhancement of the electrochemical reaction due to an increased Helmholtz-layer and electrolyte temperature is a minor effect as long as the large SCR of the low doped Si hinders an inhomogeneous dissolution of the surface and therefore the pore growth. This tendency of the SCR to improve the homogeneity is also demonstrated in SEM-photographs, showing that in low doped material the pores all start to grow at the same time, whereas in highly doped Si some pores are already growing, long before the whole area is covered with pores.

Fig. 4 demonstrates the method, that was used to analyze the SEM photographs (a). First the information is reduced to one bit: pore or nor pore (b). Afterwards the area of each pore and its surrounding free area is calculated with a self written program (c). This allows for a statistical analysis to calculate the mean values and distribution functions of the radius r_p and lengths d_p of the pores as well as the distances a_p between the pores and the density of pores N_p. We find an increasing number of pores with doping as is shown in Fig. 5, which is in agreement with [1, 2, 3, 4], where the distance between pores is correlated with the depth of the space charge region. This SCR-model is supported for low doped material by our experimental result of an increased distance between the pores for increasing anodic bias. The SCR-model however breaks down for highly doped Si, where the distance between the pores decreases with increasing potential, showing that no longer the small SCR defines the distances between pores. In this region the nucleation of pores as well as the stable pore growth is controlled by the diffusion of the minority carriers to the pore tips and the electrochemical dissolution which defines the transfer rate of the minority carriers through the silicon electrolyte interface. The ratio of both parameters defines the distance between pores: Increasing the electrocemical reaction by a higher anodic bias (increasing the Helmholtz layer) increases the probability of small pores to capture minority carriers in comparison to large pores, which by virture of their larger area have more opportunities to capture minority carriers and therefore to grow. Since a high electrolyte temperature also increases the electrochemical dissolution rate, our experimental results in Fig. 6 of an higher density of pores for increasing temperature (independent of the doping) support the above interpretation.

4 Summary

Combining

- the stabilization effect of space charge region, for the highly doped silicon
- the diffusion of minority carriers within the silicon bulk,
- the electrochemical reaction rate for Si dissolution,

we propose a mechanism for macropore formation, which can explain our experimental data on the temperature, doping and potential dependence of "random pores" in the pore nucleation phase as well as in the stable growth phase. For further application using small macropores in a submicron range the missing stabilization efficiency of the SCR may become a problem for the generation of stable pore arrays.

References

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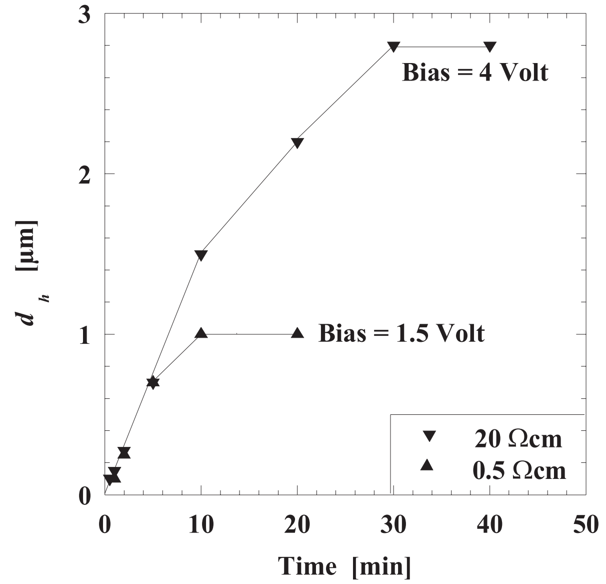

Figure 1: The thickness d_h of a homogeneously dissolved Si-layer is ploted as a function of time and doping level. When the thickness reaches its plateau value the nucleation of pores is completed.

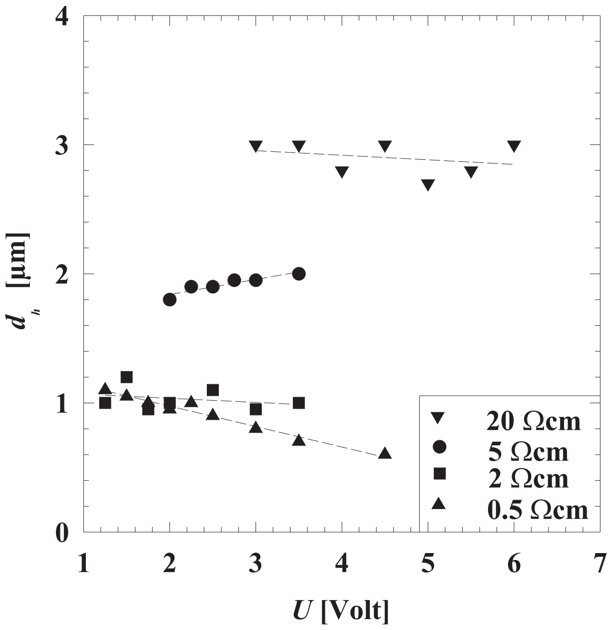

Figure 2: The dependence of the plateau value of the thickness d_h of a homogeneously dissolved Si-layer is ploted as a function of anodic potential and doping level (Temperature = 20°C).

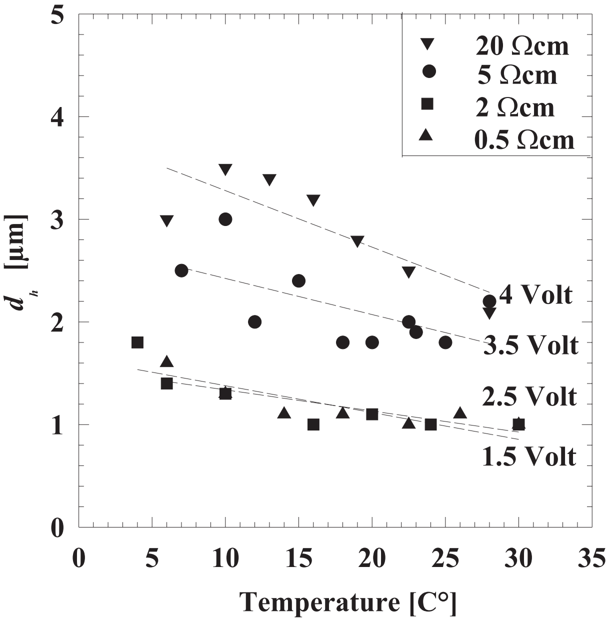

Figure 3: The influence of the temperature on the thickness d_h of a homogeneously dissolved Si-layer for different doping levels.

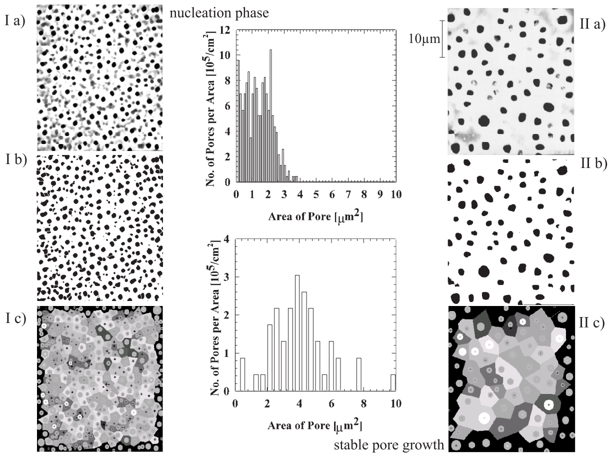

Figure 4: Statistical analysis of the lateral pore distribution in the nuleation phase I and the phase of stable pore growth II. The information of the SEM photograph (a) is reduced to one bit (pore or not pore) (b). For each pore the area and the surrounding free area is calculated (c), allowing e.g. to calculate the distribution of the size of randomly grown pores.

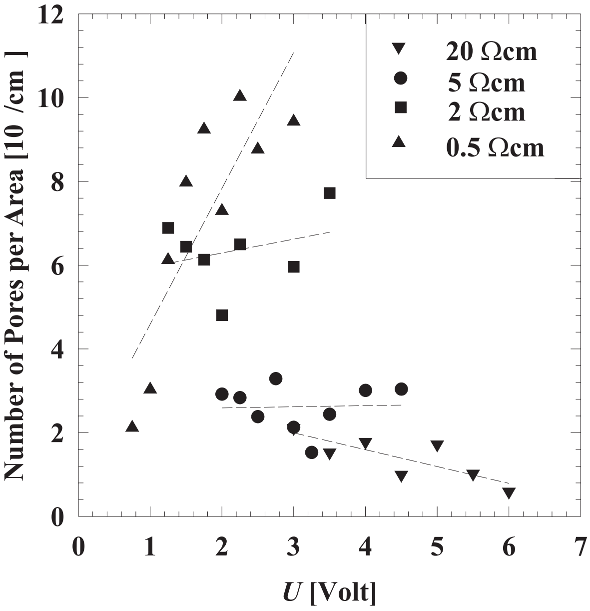

Figure 5: Density of pores as a function of the anodic potential U_{an}. For highly doped material the number of pores is growing with increasing U_{an} while for low doped Si the number decreases due to the large SCR.

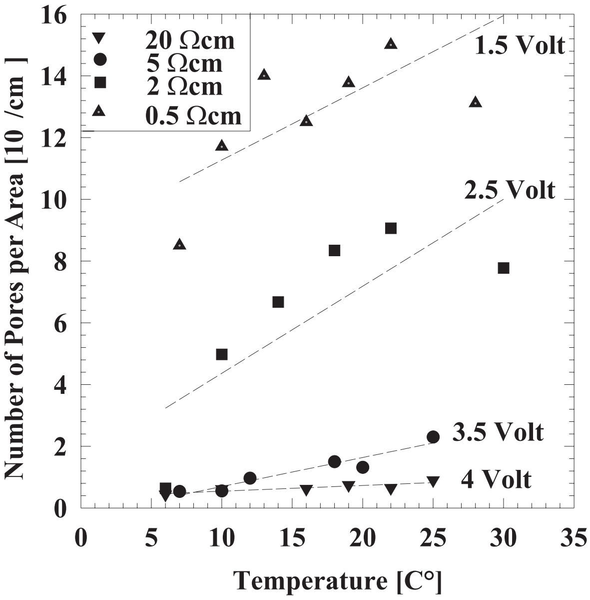

Figure 6: Dependence of the density of pores on the electrolyte temperature and dissociation for different doping levels.