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Low temperature hydrogenation of dislocated Si

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Abstract

The effect of wet chemical etching and subsequent annealing on the electrical activity of the dislocation-related centers in n-type Si is investigated by the deep-level transient spectroscopy. It is observed that hydrogen penetrates into the samples already during room temperature etching but passivates the dislocation centers only after 300°C annealing. The different dislocation centers exhibit different efficiency of hydrogen passivation. Possible reasons for the observed peculiarities of the dislocation passivation are discussed. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The study of hydrogen interaction with extended defects has great practical importance. In addition, the systematic investigations supply data about the mechanism of hydrogen passivation of electrically active point and extended defects. Finally, studies of hydrogen–dislocation interaction result in a better understanding of the nature of the dislocation electrical activity itself.

The hydrogen interaction with extended defects is studied already for more than 20 years. Hydrogen was shown to passivate the acceptor action of dislocations in n-type crystals and to decrease the intensity of the dislocation photoluminescence (PL) [1]. Later investigations showed that different dislocation bands exhibited a different decrease [2] and even an increase [3] of the PL intensity due to the treatment with hydrogen. Further, hydrogen was shown to suppress the dislocation deep-level transient spectroscopy (DLTS) signal at temperatures about 400°C [4–6] and to decrease the dislocation electron beam induced current (EBIC) contrast [7]. However, as observed in [6], hydrogen penetrates into Si at room temperature but does not passivate the dislocation electrical activity. Thus, in spite of long time investigations, some aspects of the hydrogen–dislocation interaction still remain unclear.

The difference between the experimental results described in the literature can be related to the different conditions of plastic deformation and/or hydrogen treatment. For example, Cu contamination was shown [2] to change essentially the efficiency of the subsequent hydrogen passivation. It is well established now that hydrogen can be introduced into Si at room temperature during wet chemical etching and this procedure is now widely used in the investigations of hydrogen–point defect interaction [8–11]. It seems promising to use such passivation procedure also for the study of low temperature passivation of dislocation related centers. Chemical etching avoids the surface damage and makes the hydrogenation procedure more reproducible.

The purpose of the present paper is to study the effect of hydrogen on the electrical properties of dislocations in the temperature range for hydrogenation from room temperature to 300°C. It is shown that dislocation centers with the energy levels in the upper half of the gap are not passivated after chemical etching at room temperature. An additional annealing up to 300°C is necessary to passivate them. Different dislocation centers are passivated at different temperatures and have different depth profile after passivation.

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2. Experimental

Silicon samples cut from n-type single crystals grown by the Czochralski method with the phosphorus concentration 1.2×10^{14} cm^{-3} were used in our investigations. The well defined dislocation structure with dislocation densities in the range 10^{5}–10^{7} cm^{-2} was obtained by scratching the {111} face of the samples along the <110> direction and subsequent deformation by four-point bending around the <112> axis at 625°C. The dislocation density was determined by counting the dislocation etch pits on the {111} surface. The deformation procedure was described in more detail elsewhere [12]. Hydrogen was introduced in dislocated samples during wet chemical etching in the acid solution HF:HNO_3 (1:7) at ambient temperature. Etching rate was about 4 μm min^{-1}. Some samples were annealed for 30 min at 150–300°C. Schottky contacts were formed by thermal evaporation of gold. Ohmic contacts were produced by scratching the back side of the samples with the eutectic InGa alloy.

Capacitance measurements were performed using a 1 MHz capacitance meter. The concentration of deep level centers was measured by the DLTS technique using a lock-in amplifier as a correlator. Spatial distribution of the deep-level centers was determined from the DLTS curves taken at different reverse bias and filling pulse amplitudes.

3. Results

The deformation procedure described above introduces in n-type Si the well-known deep-level spectrum consisting of four DLTS peaks (from A to D, after [13]). In addition, some energy levels in the lower half of the gap are known [14] to be introduced due to deformation under such conditions. In the present work, we will discuss mainly the B and D centers, which dominate the DLTS spectra. The depth distribution of these centers measured by the variation of reverse and filling pulse voltages is found to be practically uniform (Fig. 1). It is expected, however, that hydrogen penetrates into the crystal during etching as it was found in numerous investigations of silicon samples containing point defects [8–11]. To check if hydrogen indeed penetrates into the dislocated samples during such treatment, the Schottky diodes were prepared also on samples, which besides dislocations contain radiation defects which were introduced by irradiation of dislocated samples with high-energy (5 MeV) electrons. It is known [15] that the oxygen–vacancy pairs (V–O centers) can be partially passivated by hydrogen during chemical etching. Indeed, in the dislocated samples the decrease of the V–O center concentration is observed in the near surface region just after room temperature etching (Fig. 1). This is an evidence for the hydrogen penetration into the subsurface layers of the studied samples.

If the chemically etched samples are annealed at 150°C before the Schottky diode formation, the V–O center concentration decreases further but the concentration of the dislocation-related centers remains practically unchanged (Fig. 1). A noticeable passivation of the dislocation related centers is observed only after 300°C annealing (Fig. 1) while the V–O centers almost disappear in the near surface region after 270°C annealing.

The dislocated silicon samples were treated also in an electron cyclotron resonance (ECR) driven hydrogen plasma (the samples were previously chemically etched). Under such treatment the sample temperature did not exceed 100°C. This low temperature plasma treatment was shown earlier to be very effective in the passivation of the gold electrical activity [8]. After such a treatment a significant passivation of the dislocation related centers is observed (Fig. 2). Note also an increase of the B and D center concentrations at some intermediate depth. The C–V measurements on the samples with the high enough dislocation density show that the total decrease of free electron concentration is much higher than the sum of the concentration of the deep levels revealed by the DLTS. This behaviour is in agreement with the well-known fact that some other acceptors are introduced by plastic deformation [14]. After the ECR hydrogen plasma treatment, this acceptor action of dislocations decreases. Subsequent annealing at 300–400°C results in the further passivation of the B and D centers and partial restoration of the dislocation accep-

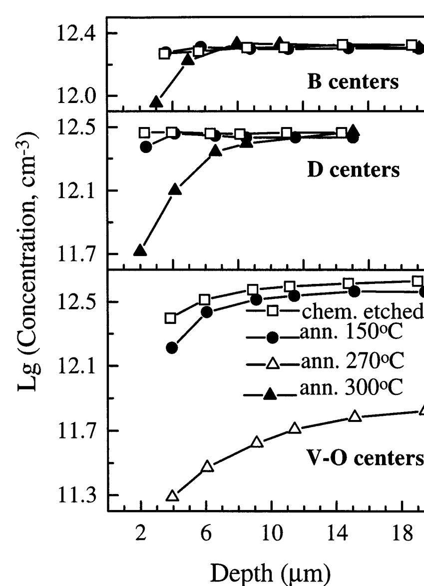

Fig. 1. Depth profile of B and D dislocation-related centers and V–O centers in plastically deformed and irradiated with 5 MeV electrons n-Si just after chemical etching and after subsequent annealing.

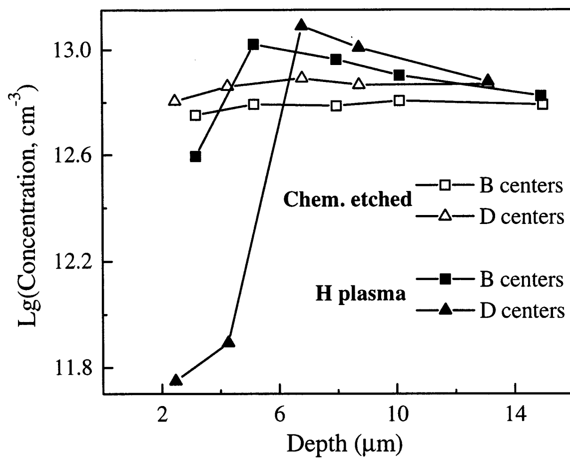

Fig. 2. Depth distribution of D and B centers in plastically deformed Si before and after treatment in the ECR plasma.

tor activity. Annealing at 600°C for 30 min practically restores the initial (before hydrogenation) electrical activity of all dislocation-related centers indicating the hydrogen out-diffusion at this temperature.

4. Discussion

The data presented show clearly that at least B and D dislocation-related centers are practically not passivated by hydrogen during wet chemical etching at room temperature although hydrogen penetrates into the crystal and passivates other defects (e.g. vacancy–oxygen pairs). The passivation of the B and D centers occurs only after subsequent annealing at 300°C. From the ECR results we obtained the different temperature dependence of passivation of the acceptors in the lower half of the gap and the B and D centers. In addition, it is seen both in Figs. 1 and 2 that the D center passivation is always more significant than that of the B centers. The increase of the measured B and D center concentration at the intermediate depths in Fig. 2 can also be easily explained under the assumption that the passivation of the deep dislocation acceptors is more effective than that of the B and D centers and occurs at larger depth. This will lead to a decrease of the potential barrier around dislocations and (in accordance with [12]) to an increase of the number of dislocation centers which are filled during the DLTS measurements.

With the reasonable assumptions given in [15], the hydrogen distribution after chemical etching can be described as

$$[\mathrm{H}] = H_0 \exp(-x/L) \tag{1}$$

where H_0 is the hydrogen concentration at the surface and the characteristic length L is determined both by the diffusion parameters of hydrogen and the etching rate. The concentration $[N]$ of the non-passivated defects can be described as

$$[N] = N_0 \exp\{(-4\pi D r_0 L/iV) H_0 \exp(-ix/L)\} \tag{2}$$

where r_0 is the radius of hydrogen capture by the defect, D is the hydrogen diffusion coefficient, N_0 is the initial defect concentration and i is the number of hydrogen atoms which should be captured by the defect to change its electrical properties. In Fig. 3 the distribution of non-passivated B and D centers is presented in the corresponding coordinates. It is seen that the depth profile of the D centers is perfectly described by the equation Eq. (2) with characteristic depth $L = 2.9$ µm. The accuracy of the B center concentration measurements is not sufficient but the data available tentatively show an approximately 2 times shorter characteristic depth. This could be interpreted as an indication that two hydrogen atoms are needed to form a stable electrically inactive complex with the B centers [15]. In any case, the points for the B center in Fig. 3 are below those for the D center indicating lower passivation efficiency for the B center.

It should be noted that Eqs. (1) and (2) are derived for the hydrogen diffusion and defect passivation during wet etching (i.e. under the conditions of moving boundary) while the data in Fig. 3 are measured on annealed samples. In this case, such spatial distribution could be explained by the kinetics of the hydrogenation process. Some other traps (say X traps) could form complexes with hydrogen during etching in accordance with Eqs. (1) and (2) and prevent hydrogen to be trapped by the B and D centers. Annealing at higher temperature leads to the dissociation of these complexes, and released hydrogen interacts with the B and D centers without significant spatial redistribution. The depth of B and D centers passivation is very similar in irradiated and non-irradiated samples, i.e. the passivation of the V–O centers as well as the macroscopic

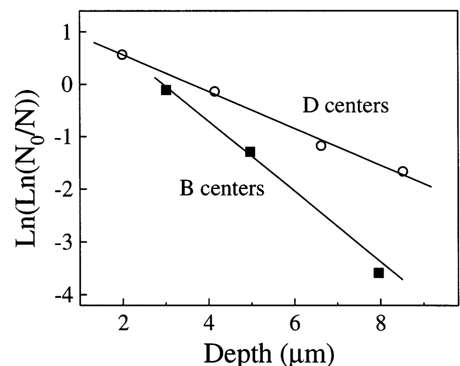

Fig. 3. Depth distribution of B and D centers presented in the scale corresponding to Eq. (2) after chemical etching and subsequent annealing at 300°C for 30 min.

hydrogen distribution is not very much affected by the X-traps. This behaviour indicates that both the X-traps and B and D centers are located only in a close vicinity of dislocations. The X-traps will not influence the hydrogen penetration but strongly effect the passivation of the B and D defects. The X-traps could be associated with the dislocation acceptor states in the lower part of the gap because these acceptor states were observed to release hydrogen approximately at the same temperature at which the B and D centers passivation effectively occurs. Our results do not exclude the existence of some energy barrier for the hydrogen–defect interaction as was proposed in [6]. However, it would be difficult in this case to explain the spatial distribution of the D centers in Fig. 3.

The significant passivation of the B and D dislocation centers at much lower temperature during an ECR plasma treatment Fig. 2 could be explained by a light induced change of interacting defects charge state. An ECR plasma treatment could also lead to a saturation of the X-traps due to the higher concentration of hydrogen penetrated into the crystal from the plasma source.

Acknowledgements

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