

Photovoltaic Characterization of Si and SiGe Surfaces Sonochemically Treated in Dichloromethane

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It is well known that the near-surface recombination and trapping of photoexcited free carriers significantly affect the photovoltaic performance. Passivation techniques are therefore in great demand for current photovoltaic technologies. Different aspects of the surface passivation in Si and SiGe were widely addressed. It was particularly concluded that sonochemical surface treatments, e.g. in chloroform (CHCl_3), can significantly improve the photovoltaic response. It is shown in this work that another reactive surface etchant containing carbon, dichloromethane (CH_2Cl_2), placed into the sonochemical reactor can effectively modify the surface photovoltaic response of Si and SiGe surfaces. X-ray diffraction studies revealed that the Si-Ge alloy layer exhibits solid solutions of Si in Ge (approximately 59 % of Si atoms) and Ge in Si (approximately 90 % of Si atoms). An order of magnitude larger photovoltaic signal, which is accompanied by slightly prolonged decay times, is observed in single crystal Si. A 50 % increase in the photovoltaic amplitude is reproduced in SiGe. In contrast to Si, sonochemical treatment of the SiGe surface tends to speed up the short-term component and slow down the long-term component of the double-exponential surface photovoltage signal. As dichloromethane acts as a carbon source, it can be suggested that sonochemically decomposed carbon atoms can effectively passivate silicon dangling bonds. We believe this sonochemical treatment step can be used for the surface passivation in manufacturing Si- and SiGe-based solar cells.

Keywords: SiGe, Photovoltage, Surface passivation, Sonochemistry.

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1. INTRODUCTION

Passivation techniques for silicon surfaces are in great demand, e.g. in solar cell technologies [1]. Currently, the mainstream method of improving the passivation effect lies in depositing a passivation film on the surface of the silicon wafer. The interface states originate from silicon dangling bond defects in the thin epitaxial layer with a thickness of several Å above the surface of the silicon wafer. These dangling bonds form a number of trap levels in the band gap, resulting in recombination losses of minority carriers [2]. Oxide-Nitride (ON) stacks have been extensively used in high efficiency solar cells as an anti-reflection coating and a passivation layer [3]. The formation of Si–O bonds was shown to suppress unwanted growth on the silicon surface during the deposition of α -SiO_xH and thus excellent passivation was achieved [4].

Though Ge, like Si, is a group IV element, their etch rates can significantly differ from each other. Thus, in oxidizing solutions, such as ozonated water (H_2O_2), Si forms a thin (1-1.2 nm) layer of passivating oxide (SiO_2). In non HF-containing solutions, the etch rate of Si is limited by SiO_2 . On the other hand, GeO_2 is water-soluble, so with the oxidation of Ge and etching of GeO_2 a net etch of Ge forms. As a consequence, in a particular solution, when Si just makes a passivation layer, Ge can be etched at a rate of 4 nm/min. Furthermore, Ge can be etched in hot water, H_2O_2 , $\text{HCl}:\text{H}_2\text{O}_2$, and $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$, unlike Si. Conclusively, solutions, which are safe for processing of silicon, are not always safe for Ge.

Different aspects of the surface passivation in Si and SiGe were previously addressed [5-13]. In particular, it was shown that the sonochemical treatments in

chloroform (CHCl_3) considerably improve the surface photovoltaic (SPV) response [14]. Considerably longer decay times and greater SPV signals were observed in SiGe and amorphous-Si/SiGe thin layers grown on Si.

In this work, we show that the SPV signal in Si can be significantly enhanced due to sonochemical treatments in dichloromethane (CH_2Cl_2). Similar effect can be observed for SiGe surfaces, although the size of the enhancement is much smaller. It can therefore be suggested that such a sonochemical treatment step would be beneficial for the surface passivation in Si- and SiGe-based solar cell fabrication processes.

2. EXPERIMENT

Several sample sets were used in the experiments. The samples had a rectangular form with a transverse size of 10×10 mm and a thickness of 300 μm . Silicon samples were manufactured from a standard single crystal silicon (*c*-Si) wafer, which was (100) oriented.

The samples with a SiGe layer were grown using similar *c*-Si (100) wafers with a thickness of 300 μm as a substrate. Standard CVD method utilizing $\text{SiH}_4/\text{GeH}_4/\text{H}_2$ at a temperature of 500 °C and a pressure of 200 Pa was used. Before deposition of the SiGe layer, the native oxide at the surface of Si substrate was removed by H_2 taken at 1000 °C. The thickness of the resulting SiGe layer was 100 nm.

The structure, morphology and the chemical structure of the SiGe specimen were determined using X-ray diffraction (XRD).

Just prior to performing sonochemical treatments, the surfaces of all samples were etched for 5 min in a 40 % HF solution. As a result of such a procedure, an

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oxide layer was removed from the sample surface and the same surface conditions were maintained before the following sonochemical treatment. In order to exclude the formation of an oxide layer on the sample surface after the HF etching and the sonochemical treatment, the samples were dried in an argon flow and were maintained in an argon atmosphere up to the beginning of the measurement.

The SPV transients were measured in the capacitor arrangement using a standard method [15]. To provide the near-surface generation of non-equilibrium charge carriers, light pulses with a 5 μ s width from a peak-wavelength of $\lambda = 405$ nm light-emitting diode (LED) were used.

3. RESULTS AND DISCUSSION

XRD studies performed on non-monochromatized Cu α radiation do confirm that the orientation of the Si substrates used here is (100). Studies done in the diffraction angles (2θ) = 25-100° do not detect any diffraction maxima, apart from the Si (400) one. Fig. 1 shows a fragment of the diffraction pattern within the angle range (2θ) = 67-72°, illustrating that a rather intense doublet belonging to this Si diffraction maximum is clearly visible. The doublet occurs due to the two components, a_1 and a_2 , in the characteristic spectrum with the wavelengths $\lambda_1 = 0.15405$ nm and $\lambda_2 = 0.15443$ nm, respectively.

The parameter of the Si unit cell (determined by the position of the diffraction maximum components) is equal to $a = 0.54299$ nm, which has only the 8-10⁻⁵ nm difference from the tabular value of this parameter ($a = 0.54307$ nm). Such differences are consistent with both the experimental errors in position determination and may be due to the effect of dopants.

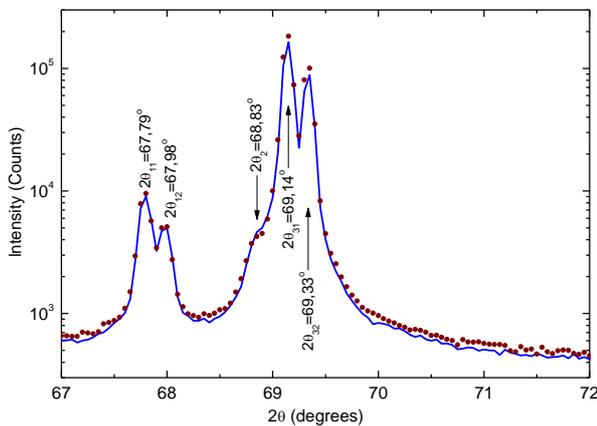


Fig. 1 – XRD diagrams around the most intense lines of the SiGe on Si films taken before (line) and after (points) sonochemical treatment

In this fragment we can see one more doublet having much less intensity, and a shoulder at the base of the diffraction maximum (400) Si, which is thought to be the consequence of imposing another doublet on the Si substrate maximum of high intensity. Confirmation of this explanation (the presence of three separate maxima) is quite clearly seen on the "naturally" monochromatic β -radiation ($\lambda_\beta = 0.13922$ nm for Cu), which is always pre-

sent in the characteristic X-ray spectrum of different elements. A fragment of the diffraction picture, which occurs near the (400) Si maximum, is shown in Fig. 2. In this case, we see a clearly evident presence of three diffraction maxima with relative intensities consistent with the relative intensities of the α -components (Fig. 1).

Therefore, beside the pronounced diffraction maximum of a single *c*-Si, two subsidiary maxima occur that are due to the Ge film. Assuming that they come from the same (400) crystal planes, the lattice parameters of the film structure are $a_1 = 0.55247$ nm and $a_2 = 0.54531$ nm.

The value $a_1 = 0.55247$ nm is less than the parameter of the bulk Ge unit cell ($a_{Ge} = 0.56576$ nm), and the value $a_2 = 0.54531$ nm is only somewhat greater than the cell parameter value of Si ($a_{Si} = 0.54307$ nm). Considering that the Si-Ge alloy system typically exhibits a set of continuous solid solutions in the whole concentration range, we can therefore suppose that the structure with the parameter a_1 is a solid solution of Si in Ge, and the structure with the parameter a_2 is a solid solution of Ge in Si.

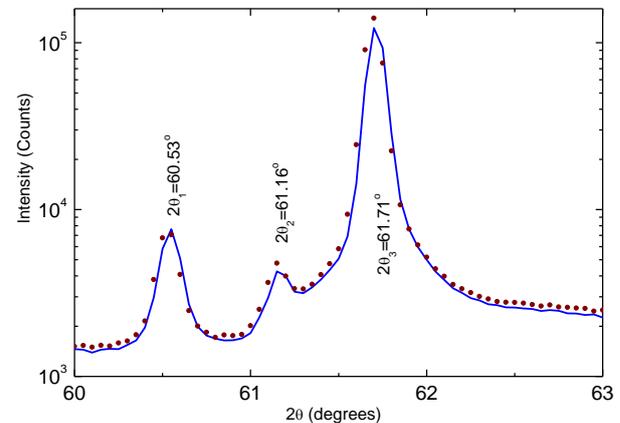


Fig. 2 – The same as in Fig. 1 taken with the monochromatic β -radiation

Since, according to [16], the change in the cell parameters in the Si-Ge system can be approximated by the Vegard rule (slight deviations will be neglected), it is possible to evaluate the alloy components. Thus, the structure with the parameter a_1 must contain approximately 59 % of Si atoms, whereas the one with a_2 must contain approximately 90 % of Si atoms.

It is seen in Fig. 1 and Fig. 2 that, after the sonochemical treatment, the positions of the diffraction maxima and their relative intensities remain practically the same. Minor differences between the peak positions observable in Fig. 1 and Fig. 2, in particular, a non-significant shift of all maxima comparable with the magnitude of the scanning step can all be related to the slight misorientation of the sample when fixing it back into the X-ray apparatus after its ultrasonic treatment. It should be noted that a non-detachable control sample gave essentially the same results in the course of repeated XRD studies.

It is known that, in general case, the SPV signal is determined by the composition and concentration of electrically active semiconductor surface defects. One can expect that after the etching and sonochemical treatment of the samples the composition and concentration

of electrically active defects can considerably change. Consequently, the SPV should also substantially alter.

In this work, after each treatment step of the sample surface, the SPV decay curves were measured. In every case, the SPV decay time and the amplitude value of the SPV signal undergo significant changes.

As stated above, prior to each sonochemical treatment step, the sample surfaces were etched in a 40 % HF solution. To be sure that such a treatment consistently provides the same surface condition, we have tested the SPV decay curves in Si and SiGe/Si samples, which were cyclically etched several times in a 40 % HF solution. These measurements have revealed that the SPV decay curves measured after each etching step were reproduced with high accuracy.

The SPV decay curves taken from the surface of single *c*-Si are shown in Fig. 3. Here, curve 1 corresponds to a sample of monocrystalline Si whose surface was only etched in a 40 % HF solution for 5 min. However, if the sample surface was subjected to the subsequent sonochemical treatment in dichloromethane for 1 min (curve 2), then the amplitude of the SPV signal increases significantly. At the same time, increase in the duration of sonochemical treatment in dichloromethane to 5 min leads to the same changes in the amplitude of the SPV signal (curve 3).

The obtained curves were fitted to two decreasing exponents as

$$U_{pv} = A_1 \cdot \exp(-t/t_1) + A_2 \cdot \exp(-t/t_2) + U_0. \quad (1)$$

The resulting fitting of the parameters is shown in Table 1. The analysis of the obtained data shows that sonochemical treatment in dichloromethane for 1 min causes an increase in the amplitude value of the SPV signal by more than 10 times, which is accompanied by slightly prolonged decay times. Treatment for 5 min remains this effect nearly the same with a slight decrease in the SPV amplitude and decay times.

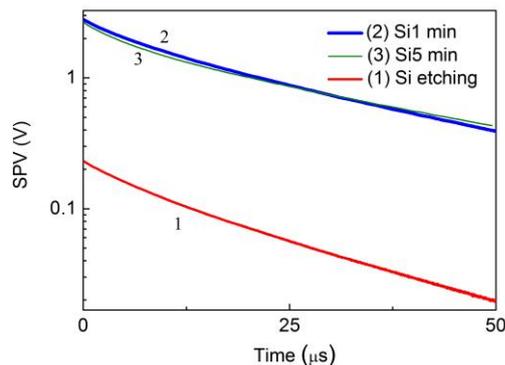


Fig. 3 – SPV decays from Si surfaces: HF-etched (1), sonochemically treated in dichloromethane for 1.5 (2) and 5 (3) min

Table 1 – The fitting parameters in Eq. (1) for the experimental SPV decay curves 1-3 shown in Fig. 3

	1) Si, HF etching	2) Si, 1 min sonication	3) Si, 5 min sonication
$t_1, \mu\text{s}$	23.37	28.92	27.02
$t_2, \mu\text{s}$	6.29	6.32	4.5
U, V	0.23	2.8	2.66

Fig. 4 shows the decay curves of the SPV signal detected from the surface of the SiGe layer. Similar to Fig. 3, curve 1 in Fig. 4 shows the kinetics of the SPV signal in a sample with the SiGe layer, only etched in a 40 % HF solution for 5 min. In contrast to single *c*-Si, the subsequent sonochemical treatment of the surface of this sample in dichloromethane for 1.5 min (curve 2) results only in a slight change in the amplitude of the SPV signal. With an increase in the duration of sonochemical treatment in dichloromethane up to 5 min (curve 3), the SPV signal amplitude does not change at all. The decay curves for this sample were also analyzed by fitting to Eq. (1). The approximation parameters of the experimental curves are shown in Table 2. In contrast to single *c*-Si, sonochemical treatment in the sample with the SiGe layer for 1.5 min and for 5 min speeds up the short-term component t_2 and slows down the long-term component t_1 of the SPV signal.

The data of Fig. 3 and Fig. 4 can be explained as follows. As stated above, the passivation rates for Ge and Si surfaces differ from each other quite significantly. As a consequence, the resulting SPV signal in Si and SiGe samples exhibits different behavior upon treatments in dichloromethane. The bubbled dichloromethane is suitable to act as a reactive surface etchant as well as a source of additional carbon. This triggers the formation process of Si–C bonds at the Si and SiGe surfaces. Therefore, one can suggest that carbon atoms released from dichloromethane molecules during sonochemical dissociation, passivate only silicon dangling bonds. So that the SiGe surface remains much less passivated during the sonochemical treatment.

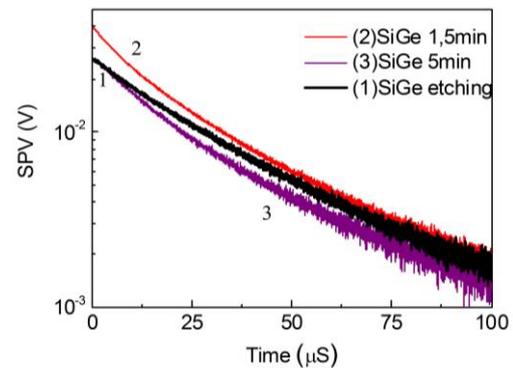


Fig. 4 – SPV decays from SiGe surfaces: HF-etched (1), sonochemically treated in dichloromethane for 1.5 (2) and 5 (3) min

Table 2 – The fitting parameters in Eq. (1) for the experimental SPV decay curves 1-3 shown in Fig. 4

	1) SiGe etching	2) SiGe 1.5 min sonication	3) SiGe 5 min sonication
$t_1, \mu\text{s}$	27.32783	30.60176	43.73953
$t_2, \mu\text{s}$	27.32757	8.13618	14.87734
U, V	0.02632	0.03982	0.02589

4. CONCLUSIONS

In summary, the paper shows that SPV signal in Si can be significantly enhanced due to sonochemical treatments in dichloromethane. A similar effect can be observed for SiGe surfaces with a smaller enhancement. An order of magnitude larger SPV signal is observed in

Si, whereas a 50 % increase in the amplitude is reproduced in SiGe. It can be suggested that dichloromethane acts as a carbon source, so that sonochemically decomposed carbon atoms can effectively passivate silicon dan-

gling bonds. It is furthermore believed that such a sonochemical treatment step would be beneficial for the surface passivation in Si- and SiGe-based solar cell fabrication processes.

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Фото-ЕРС на поверхнях Si та SiGe при сонохімічній обробці у дихлорметані

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Процеси рекомбінації та захоплення електронів і дірок через поверхневі центри рекомбінації та захоплення суттєво впливають на ефективність різних фотоелектричних пристроїв. Через це у процесі виробництва таких пристроїв значну увагу приділяють пасивації поверхонь. Різні аспекти пасивації поверхні Si та SiGe достатньо широко розглянуті в літературі. Зокрема, показано, що сонохімічна обробка поверхні, наприклад, в хлороформі (CHCl_3), може значно покращити фотоелектричний відгук. У даній роботі показано, що й інший карбон-місткий реакційноздатний поверхневий травник, дихлорметан (CH_2Cl_2), використаний у сонохімічному реакторі, може ефективно впливати на величину поверхневої фото-ЕРС в зразках Si та SiGe. Дослідження рентгенівської дифракції показали, що шар сплаву Si-Ge утворює тверді розчини Si в Ge (що містить приблизно 59 ат. % Si) та Ge в Si (наближено 90 ат. % Si). У монокристалічному Si отримано збільшення на порядок величини сигналу фото-ЕРС із трохи затягнутою кривою її релаксації. В SiGe це збільшення фотовідгуку складає біля 50 %. На відміну від Si, сонохімічна обробка поверхні SiGe веде до прискорення короткочасної компоненти та уповільнення довготривалої складової сигналу поверхневої фото-ЕРС, що описується подвійною експоненціально спадаючою функцією. Оскільки дихлорметан виступає в якості джерела вуглецю, можна припустити, що звільнений при сонохімічній обробці вуглець ефективно пасивує вільні кремнієві зв'язки. На наш погляд, сонохімічна обробка має потенціал використання для пасивації поверхонь у виробництві сонячних батарей на основі Si та SiGe.

Ключові слова: SiGe, Фото-ЕРС, Пасивація поверхні, Сонохімія.