

## Impact of Hydrogenation on Electrical Properties of NiSi<sub>2</sub> Precipitates in Silicon

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**Abstract.** Influence of annealing in molecular hydrogen as well as of treatment in hydrogen plasma (hydrogenation) on the electrical properties of NiSi<sub>2</sub> precipitates in n- and p-type silicon has been studied by means of deep level transient spectroscopy (DLTS). Both annealing and hydrogenation gave rise to noticeable changes of the shape of the DLTS-peak and of the character of its dependence on the refilling pulse duration that according to [1] allows one to classify the electronic states of extended defects as “*band-like*” or “*localized*”. In both n- and p-type samples DLTS-peak in the initial as quenched samples showed *band-like* behaviour. Annealing or hydrogenation of n-type samples converted the *band-like* states to the *localised* ones but differently shifted the DLTS-peak to higher temperatures. In p-type samples, the initial “band-like” behaviour of DLTS peak remained qualitatively unchanged after annealing or hydrogenation. A decrease of the DLTS-peak due to precipitates and the appearance of the peaks due to substitutional nickel and its complexes were found in hydrogenated p-type sample after removal of a surface layer of 10-20µm.

### Introduction

The impact of the hydrogenation on the electrical properties of transition metal impurities was intensively investigated during last decade. To the best of our knowledge all of the published papers were devoted to the study of metals dissolved in silicon [2-4] matrix but there is no one dealt with the metal precipitates. Meanwhile, the information about the impact of the hydrogenation on the electric properties of transition metals precipitates is of great interest for the photovoltaic industry which uses low-cost multicrystalline silicon containing the precipitates of different composition.

Nickel belongs to the fast-diffusing 3d transition metals in silicon that properties are rather well understood [5]. Being in dissolved substitutional state it forms three levels in the silicon band gap: one double acceptor, one acceptor state and a donor state [5]. Hydrogenation by means of the remote plasma treatment produced a dramatic reduction in electrical activity of these deep levels [4], while the incorporation of hydrogen by wet chemical etching introduced up to 6 new Ni-hydrogen related levels [6]. By proper chosen sample preparation conditions nickel-silicide nanoprecipitates could be grown in silicon matrix. Their atomic structure and electric properties in n-type material were well established by means transmission electron microscopy (TEM) and deep level transient spectroscopy (DLTS) [1,7-9].

In this work we report the first results of our DLTS study of hydrogenated nickel-silicide precipitates in n- and p-type silicon.

## Experimental Details

We used the samples of the n- and p-type Fz Si doped of about  $10^{15}$  atoms/cm<sup>3</sup> with phosphorus and with boron respectively. For in-diffusion Ni was evaporated on the (100) or (111) oriented wafers. The heat treatment to saturate Si with nickel was performed in a vertical furnace in argon at the temperature 900°C for n-type samples and at 850°C for p-type samples following by quenching in 10% NaOH. Then, a surface layer of few micrometers thick was removed mechanically and chemically and one part of the samples was annealed at 310°C for 1h in molecular hydrogen, another part was treated in hydrogen remote plasma at 310°C for 1h and the remained part of the samples was not exposed by any treatment.

Schottky-contacts (Au for n-type samples, Al for p-type samples) were evaporated on chemically polished surface. Ohmic contacts were made using In-Ga eutectic. DLTS-measurements were performed with a computerized spectrometer working at a frequency of 1 MHz.

## Experimental Results

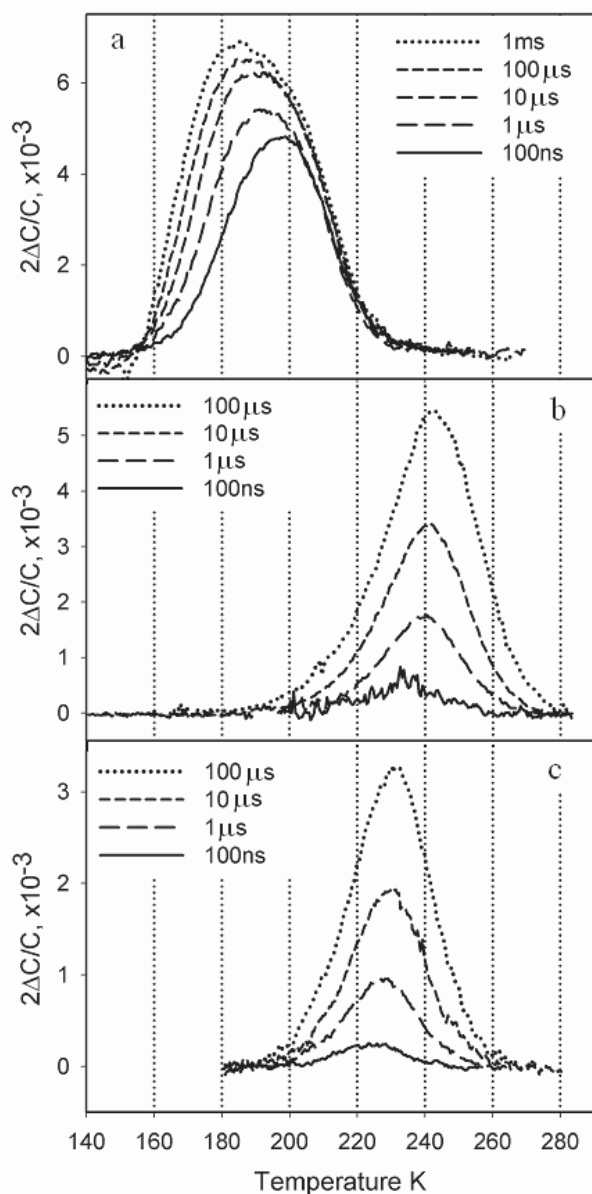
**n-type silicon.** As-quenched sample with NiSi<sub>2</sub> precipitates exhibit a broadened DLTS peak (see Fig. 1a) that temperature position and that filling behavior coincided well with the previously reported data [1]. A characteristic feature of the peak is that its maximum shifts toward the lower temperature with increasing of the filling pulse duration,  $t_p$ , while its high-temperature side is independent on  $t_p$ . According to [1], such a behavior corresponds to “*band-like states*”, i.e. to a band of electronic state with a rapid interstate exchange.

Annealing of our samples in molecular hydrogen as well as in the hydrogen plasma changed the temperature position, the shape and the refilling behavior of the DLTS-peak (Fig.1b and 1c). Under the filling pulse duration variation the peak shape and the position in the annealed samples remained practically unchanged but the magnitude of the DLTS signal increased logarithmically with the increasing of  $t_p$ . High temperature sides of the DLTS lines coincided after normalization with respect to the peak maximum (not shown here for brevity). According to [1], these properties correspond to “*localized states*”, i.e. to a band of electronic states without interstate exchange.

Temperature position of DLTS peak of our annealed samples shifted approximately for 40K towards higher temperatures and coincided well with the final position reported for the samples annealed in a inert ambient at the same temperature [7] that was reached in [7] after the annealing durations of about 12 minutes.

The temperature position of the DLTS peak in hydrogenated sample lies between the position of initial and that of annealed sample. According to the previous results [7] that position corresponds to an intermediate stage reached by the annealing at 320°C after the duration as short as 20s. Our samples were keeping for substantially longer time (1 hour) during the treatment in hydrogen plasma. So, we conclude that the presence of atomic hydrogen retarded significantly the process responsible for the shift of DLTS-peak toward higher temperature under the heat treatment.

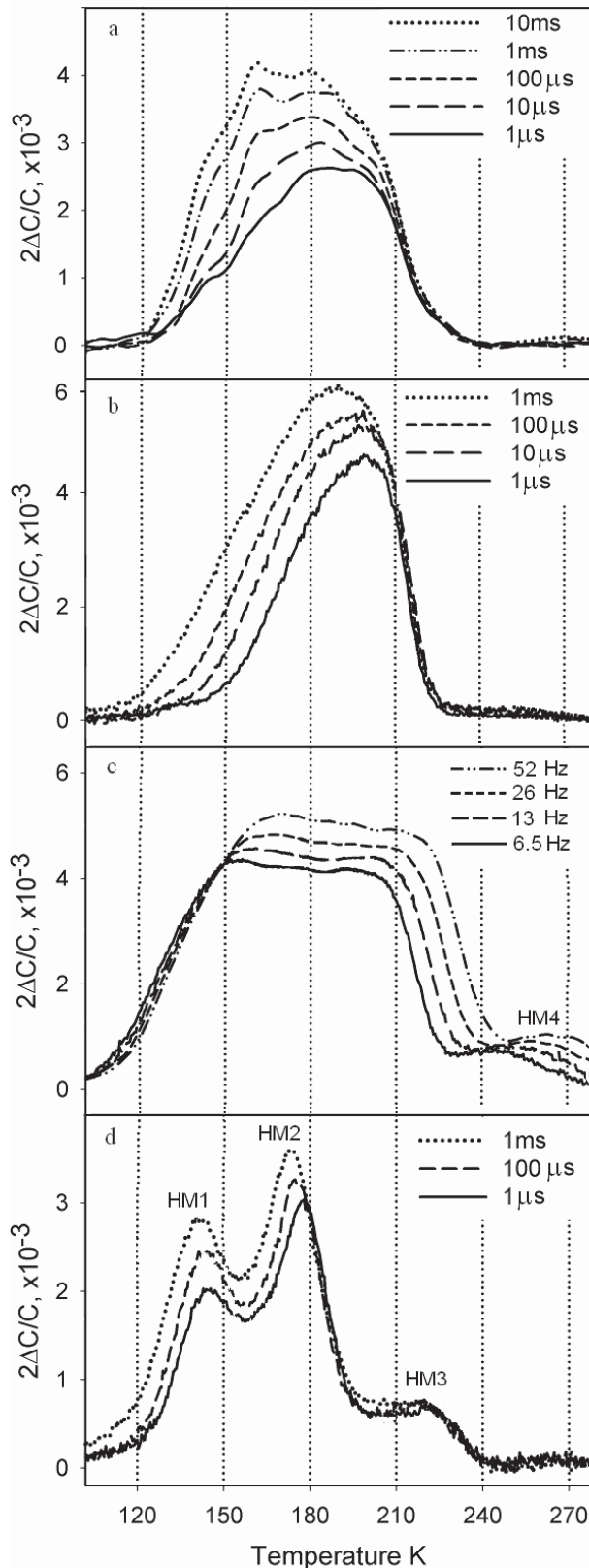
**p-type silicon.** Fig.2a,b show the sets of DLTS spectra of the as-quenched and of the annealed p-type samples obtained for different  $t_p$ . One can clearly see that the both sets exhibit properties of *band-like* defects described above for the as-quenched n-type sample: with increasing of  $t_p$ , the high temperature side of the peak remains unchanged, while the low temperature part of the peak grows up and the position of the peak center shifts toward the lower temperature. Thus, in contrast to n-type samples, annealing didn't convert the band-like states of initial nickel-silicide precipitates to the localized states.



**Fig.1:** DLTS spectra associated with NiSi<sub>2</sub> precipitates in n-type Si samples: (a) as quenched sample, (b) annealed at 310°C for 1 hour in molecular hydrogen and (c) treated in hydrogen remote plasma at 310°C for 1h. Lock-in correlation frequency  $\nu_t=32\text{Hz}$ , reverse bias - 4 V, filling pulse voltage - 3.8 V, filling pulse durations are shown in the legends.

The shape of the spectra of as-quenched p-type sample is similar to the reported earlier [10] except the presence of very small peaks around 140K, 160K and 180K in the Fig.2a upon the background of the main spectrum part. These small peaks become more pronounced when the filling pulse duration increases. After annealing at 310°C in molecular hydrogen the main broad peak narrowed, became smoother and the small peaks disappeared (Fig. 2b).

Fig.2c represents DLTS-spectrum of the hydrogenated p-type sample when the Schottky contact was evaporated after a short chemical etching that removed only few microns layer from the surface. In this case, the main DLTS peak is broader than that of the initial and of the annealed samples. Its shape is now more rectangular-like. When comparing the spectra of Fig. 2a,b,c. on the same plot one can find that the high temperature sides of all three spectra coincide. So the result of hydrogenation is an increase of low-temperature part of the spectrum and the appearance of a small peak on its high temperature shoulder marked in Fig.2d as HM4. Variation of emission rate window revealed (Fig. 2c) that the main peak shifted as a whole similar to reported previously for copper-silicide precipitate in silicon [8]. The hydrogen concentration produced by the plasma treatment is expected to decrease from the surface to the depth. In order to check whether the shape of the main peak did depend on the hydrogen concentration we removed the surface layer of a thickness of about 10-20 $\mu\text{m}$  by mechanical polishing and subsequent chemical etching.



**Fig.2:** DLTS spectra associated with NiSi<sub>2</sub> precipitates in p-type Si samples:

(a) as quenched;

(b) annealed at 310C for 1 hour in molecular hydrogen;

(c-d) treated in hydrogen remote plasma at 310°C for 1h before (c) and after (d) the removal of a surface layer of about 10-20μm.

Lock-in correlation frequency: (a,b,d)-  $\nu_t=6,5\text{Hz}$ , (c) -shown in the legend; reverse bias: (a) – 6V, (b-d)-3V, and filling pulse voltage – 2.8V. Filling pulse durations: (a,b,d)- shown in the legends, (c)-100μs.

The result of this experiment is shown in Fig. 2d. Instead of the initially rectangular-like peak (Fig. 2c) the spectrum consisted now of 2 well resolved peaks and of a high temperature shoulder. With increasing of  $t_p$ , the signal at the low temperature tails of the peaks increases logarithmically similar to the spectra shown in Fig. 2a,b. This indicated the presence of the signal from an extended *band-like* defect. The spectrum might be deconvolute in this way to a superposition of three peaks of point-like defects with the temperature position of the point-like defect peaks denoted in the Fig.2d as HM1, HM2, HM3

and a broad band of that exhibit the *band-like* behavior (not shown). The magnitude of the broad band component was found to be noticeably less than before the removal of the surface layer.

The position of the peaks HM1, HM2, HM3 and HM4 as well as small peaks found in the as-quenched sample were quite similar to the DLTS-peaks in notation [6] H(160), H(190), H(235) and H(275) respectively observed in nickel doped silicon after wet chemical etching [6]. These peaks were found to be thermally unstable and disappeared according to the data of [6] after annealing at 200°C for 1 hour. That is why we could not exclude that they might appear during the chemical etching of our samples as the result of the interaction with the traces of dissolved nickel atoms.

Indeed, capacitance-voltage (CV) measurements on all our p-type samples revealed a decrease of shallow acceptor concentration at the surface indicating the hydrogen incorporation during wet-chemical etching before contact evaporation. Additionally, in all kinds of the investigated samples we found a peak close to the temperature limit of our set-up (80K) that could be attributed to the isolated nickel donor [6]. However, no correlation was established between the nickel donor concentration and the magnitude of these peaks. In the annealed sample, for example, the nickel donor concentration could vary by order of magnitude after subsequent etching prior the contact re-evaporation but the shape and the magnitude of the spectrum presented in Fig. 2b remained unchanged. Moreover, double-DLTS profiling of the magnitude of the main point-like defect peaks HM1 and HM2 did not revealed any noticeable decrease of their concentration down to the depth where the wet-etch induced hydrogen concentration was negligible.

On the other hand, one should emphasize, that the appearance of the point-like defects HM1 and HM2 was accompanied with the decrease of the signal due to precipitates under hydrogenation. This correlation might be explained as result of a partial dissolution of nickel-silicide precipitates stimulated by hydrogen. In this case, we have to assume as well that hydrogen-nickel-related defects are not stable only close to the surface where the reaction components can easy escape to the latter.

## Summary and Discussion

Our results presented above showed that the hydrogenation by means of the remote plasma treatment changed noticeably DLTS-spectra of silicon samples containing initially nickel-silicide precipitates. Moreover, the changes of the spectra under annealing and hydrogenation differed significantly for the samples of n- and p-types. In previous works [7-9], a good correlation between the atomic structure of NiSi<sub>2</sub>-precipitates and the properties of DLTS-signal was established in n-type silicon. It was shown by TEM that Ni atoms form a plate-shaped precipitates consisting of two {111} atomic layers of NiSi<sub>2</sub> upon rapid quenching of Si crystals [7-9]. Diameter of the platelets depends significantly on the diffusion temperature, quenching rate and is expected to be about 20-30nm by our sample preparation conditions. Annealing in an inert ambient at temperature between 200°C and 400°C leads to a transformation of precipitate form into a more compact one with substantially smaller values of the strain energy of bounding dislocation and (111) interfaces. Transformation at this temperature occurs without long-range diffusion, so it is an internal ripening of precipitate. This proceeds by island formation at the border of the platelets and bounding dislocation climbs out from the platelet plane [7-9].

Rearrangement of Ni and Si atoms required for internal ripening leads to a deviation of bounding dislocation from its strictly planar configuration and, therefore, to a transformation of precipitate electronic structure. In the DLTS measurements of n-type samples this process appeared as a rapid change of electronic structure from *band-like* to *localized*, and as a shift of the whole DLTS-spectra towards higher temperature. We found that in p-type sample *band-like* behaviour remained unchanged upon annealing reflecting the conservation of the

electronic structure of the precipitates. This implies that either the precipitates in p-type are rather stable and do not exhibit such strong changes of their structure upon annealing like observed in n-type samples or the origin of their *hole* trap states in p-Si is not the same as that of the *electron* trap states in n-Si. In the latter case, the conservation of the kind of the states upon annealing in p-Si can be explained assuming that, in fact, they are the states at the precipitate boundary rather than the states of the bounding dislocation like in n-type.

The results of hydrogenation can not be explained now unambiguously. In n-type samples we observed an apparent retarding of the internal ripening process. Generally it might be caused either by a particular structural arrangement of the hydrogenated precipitate or have a pure electronic origin. In the first case, one has to assume either that the kinetics of internal ripening slows down drastically in the presence of the hydrogen or that the stable configuration of the hydrogenated precipitate differs from that in the absence of hydrogen. Since the structure transformation during internal ripening takes place on the atomic scale one needs to assume the presence of a rather large local concentration of hydrogen at or within the precipitates. In other words the precipitate must work as a huge sink for the hydrogen. In the second case, an increase of the positive charge of the precipitate due to hydrogen capture must be taken into consideration. The increase of the positive charge of the particle must induce the capture of additional free electrons from the conduction band and could give changes of the apparent emission characteristics of the defect.

In p-type samples, the significant difference between the shapes of DLTS-spectra of the annealed and of the hydrogenated sample was registered. The appearance of point-like defect peaks was tentatively attributed to a partial dissolution of nickel-silicide precipitates stimulated by hydrogenation. Observation of a similar process on an atomic scale was reported by Feklisova et al [11] where dissociation of iron-boron pairs stimulated by hydrogen was found. It was argued in [11] that the stimulated dissociation might be due to a larger binding energy of B-H pairs comparing with Fe-B pairs.

Obviously, additional DLTS and TEM investigations are needed to clear understand all details of the impact of hydrogenation on the electric properties of precipitates found in this work.

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