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OXYGEN RELATED MECHANISM OF REVERSE ANNEALING FOR BORON IMPLANTS IN SILICON

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Abstract - The review of the existing data on the reverse annealing of boron implants in silicon is given. The idea of the exchange reaction of boron substitutionals with silicon selfinterstitials as being responsible for the phenomenon is critically considered. Instead, the possible involvement of oxygen and oxygen-related secondary defects is proposed.

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Boron is the main p-type dopant currently used in the manufacture of silicon devices. Among the doping techniques ion implantation has gained wide application and so boron implanted silicon structures are commonly met.

It is a well known experimental observation that when a boron implanted silicon substrate undergoes the annealing procedure then, for a certain temperature region, a decrease of conductivity takes place. This effect is called reverse annealing. For still higher temperatures the annealing curve regains its common, increasing character until the conductivity reaches its maximum value determined by both the implantation conditions and the substrate parameters.

The existing experimental data concerning the reverse annealing[1-4] differ as to the magnitude of the conductivity drop and its temperature region of occurence. It has been found from channeling and nuclear reaction studies[1] that the decrease of conductivity may be attributed to the lowering of substitutional boron concentration -i.e. the temperature dependence of substitutional boron concentration also exhibits the reverse annealing behaviour.

The physical nature of the reverse annealing phenomenon is not fully understood neither from the experimental nor from the theoretical point of view[5]. However considerable experimental evidence has been gathered and on its basis some propositions for theoretical explanation have been put forward. It is rather generally accepted that the decrease of substitutional boron contents is achieved as the result of interaction with secondary radiation damage effects[6]. During the annealing process as large defect aggregates are being decomposed, highly mobile silicon selfinterstitials may be released. Silicon interstitials can then react with substitutional boron ions thus increasing the interstitial boron concentration.[1,3,7-10] The reaction would involve the exchange mechanism as proposed by Watkins[11]:

$$\text{defect complexes} \xrightarrow{\text{annealing}} Si_I \ ; \ B_{subst} + Si_I \rightarrow B_I$$

The question why the replacement mechanism is not active for lower temperatures

[+]Permanent address: Institute of Physics, Polish Academy of Sciences, Warsaw, Poland is usually explained by the assumption of sufficient stability of defect complexes. The incorporation of interstitial borons into the host lattice for higher temperature region would be accomplished by the reaction with thermally generated vacanties[12].

However the explanation of the reverse annealing phenomenon by the replacement mechanism alone cannot account for all the existing experimental data and hence can hardly be regarded as satisfactory. Here are some of the more important questions and problems which cannot be explained within Watkins' exchange based mechanism:

- the reverse annealing behaviour is observed only for boron implantation. It cannot be found for other implants, including here also group III elements as aluminium or thallium for which Watkins' replacement reaction is well known to occur.

- boron ions which leave the silicon host lattice within the reverse annealing temperature region do not take random interstitial positions (as they do for high temperature proton irradiation) but they appear to lie along ⟨110⟩ atomic rows[13].

- initial substitutional boron concentration in "as implanted" samples cannot be lowered by room temperature (RT) proton irradiation[1,9]. However, if the same samples undergo full annealing treatment, then considerable concentrations of boron interstitials may be created under RT proton bombardment.

- there seems to be serious mismatch between the involved concentrations of available selfinterstitials and boron substitutionals.

The last remark requires more detailed discussion because of its crucial importance. To be more specific let us consider the implantation of 10^{15} Bcm^{-2} dose with the energy of 150 keV. Then the concentration of boron ions in the implanted layer would be as high as $n_B = 10^{19}$ cm^{-3}. The estimation of available concentration of interstitials is not so straightforward. As the implanted ion comes to rest in the silicon substrate it collides many times, thus creating a large number of vacancy - interstitial pairs. However, during room temperature implantation the vast majority of the generated damage is instantly annealed. Only some point defects escape instant annihilation by forming defect clusters and those, while decomposing at the elevated annealing temperatures could release highly mobile selfinterstitials able to take part in the replacement reaction. Taking into consideration the available information on intrinsic defects in silicon[14] one may conclude that the only candidates to produce selfinterstitials in the reverse annealing temperature region would be di-interstitial complexes P6 and A5 (which are likely to transform into O2 and B3 for higher temperatures). Some of the mentioned defect centres are paramagnetic and therefore may be observed in EPR. On the basis of such studies[15] their concentration in the implanted layer may be estimated as n_I 10^{15} cm^{-3}. This concentration is small in comparison with 10^{18} cm^{-3} which would be necessary to account for the decrease of substitutional boron concentration during the reverse annealing. Furthermore, one has to remember that for implanted silicon structures the distribution of the implanted dopants does not exactly coincide with the radiation damage distribution, thus still increasing the existing discrepancy. And so, even when taking into account that there may exist other centres, not detectable by EPR, which also would be able to produce selfinterstitials it is hardly probable that the interaction of boron substitutionals with silicon interstitials alone could be responsible for the reverse annealing behaviour of room temperature boron implants in silicon.

Also Della Mea[16] while studying the interaction of radiation damage produced by Hg implantation with boron substitutionals diffused into a silicon substrate arrived at the conclusion that the replacement mechanism itself could not be responsible for the observed peculiar annealing behaviour.

Searching for other possible mechanisms which could explain the reverse annealing phenomenon one should also consider interaction with oxygen. In the reverse annealing temperature region oxygen interstitials tend to cluster and form so-called "thermal donors". Indeed the possibility that oxygen may influence the annealing process of the radiation damage is supported by a wide variety of experimental evidence. Some of that evidence is specified below:

- the presence of oxygen in the substrate was found to influence directly the annealing behaviour of the radiation damage[17].

- the reverse annealing was reported to appear in Czochralski grown silicon with high oxygen concentration. On the other hand, in oxygen lean FZ material there seems to be no evidence for its occurence[6].

- for "as implanted" samples the initial substitutional boron concentration is much higher in Cz silicon[1] than for oxygen lean material.

It is also of crucial importance to consider whether the oxygen centres could be present in sufficient concentration to meet the number of displaced boron substitutionals. Oxygen clusters known as thermal donors are created upon annealing in oxygen rich silicon in the 320°C - 500°C temperature range, their formation rate peaking at 450°C. The formation rate values are usually within $10^{11} - 10^{12}cm^{-3}s^{-1}$ range and so to obtain significant concentrations of thermal donors heat treatment must be prolonged for days. However, the implanted layer is strongly p-type ($n_B = 10^{19}cm^{-3}$) and in such material both equilibrium concentration and formation rate of thermal donors are enhanced[18]. Then even short annealing times can produce considerable numbers of thermal donors in the implanted layer. According to Wada[19] one may expect thermal donor concentrations as high as $10^{17} - 10^{18}$ cm^{-3} to be present in the implanted layer following the standard annealing treatment. Such a number would then be sufficient to account for the reverse annealing.

One may only speculate about the way in which substitutional boron contents can be influenced in the reverse annealing temperature region by the growth or by the presence of thermal donors. The possibility that acceptors might directly be involved in the creation of thermal donors has already been considered[20,21]. It receives direct experimental support since both the thermal equilibrium concentration and the formation rate of thermal donors have been found to depend strongly on acceptor concentration[19] and also they take different values for different acceptors[22]. However, such possibility was not considered in recently published theoretical models for thermal donors formation[23,24].

Nevertheless, it is possible to create the structure similar to the OBS model but with a boron atom replacing the silicon atom serving as a centre for oxygen cluster formation. For such "modified" thermal donors the flip of silicon atom into interstitial position after the arrival of the third oxygen atom would be a mechanism producing interstitials borons and thus manifestating itself as reverse annealing. This is illustrated in FIGURE 1.

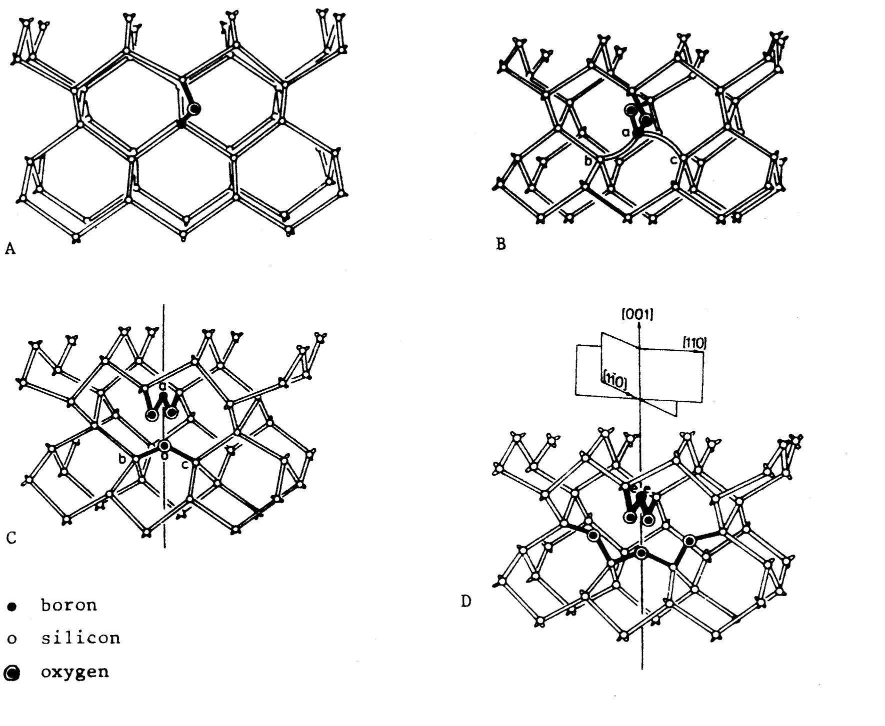

FIGURE 1. Successive phases of "modified" thermal donor formation. In phase C interstitial boron is created.

The speculative supposition that borons might be incorporated in the structure of thermal donors finds considerable experimental support in the fact that interstitial boron ions created within the reverse annealing temperature region do not take random positions but that may be monitored along $\langle 110 \rangle$ atomic rows. Such positions agree well with that predicted by the OBS model for silicon interstitials participating in thermal donors. It requires mentioning here that the suggestion that borons laying along $\langle 110 \rangle$ were not really isolated interstitials but rather part of large complexes was also put forward by Watkins[25] while discussing the G25 centre.

Also the rapid character of incorporation of boron ions into the host lattice for the temperatures above the reverse annealing region suggests that one particular defect complex is being annihilated (and preferably the complex which incorporates also boron).

On the other hand if borons would take part in thermal donors formation then also in pre-annealed samples (i.e. for temperatures lower than the reverse annealing temperature region) substitutional borons would be involved in the early stages of oxygen cluster formation (i.e. clusters with less than 3 oxygen atoms). Then, the presence of oxygen atoms in vicinity of boron substitutionals could certainly affect their sensitivity to proton irradiation[1,9].

CONCLUSIONS

It seems fairly reasonable to involve oxygen and oxygen-related complexes in the explanation of the annealing behaviour of the radiation damage induced in the silicon substrate by ion implantation. In particular there are many reasons to make it responsible for the reverse annealing of boron implants although the particular way in which oxygen and namely thermal donors could influence the lattice position of boron implants may only be speculated upon. Magnetic resonance studies of thermal donor formation in Czochralski grown silicon doped with different acceptors which are currently conducted, as well as luminescence studies of heat--treated implanted layers are expected to supply new information on the subject.

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