Comment on "Evidence for Vacancies in Amorphous Silicon"

In a recent Letter [1], van den Hoven, Liang, Niesen, and Custer address the question of whether or not the structural relaxation of amorphous silicon (*a*-Si) upon annealing is related to or caused by point-defect interaction and/or annihilation. From a ^{119}Sn Mössbauer study of *a*-Si implanted with radioactive ^{119}Sb parent isotopes to ^{119}Sn, they conclude: "*These data are the first local structure evidence indicating the existence of point defects in a-Si that are analogous to crystal vacancies.*"

It is the purpose of this Comment to point out the following. (1) This interpretation of the main results from their experiment is not sound; i.e., this part of the data does not give the evidence claimed. (2) Previous ^{119}Sn Mössbauer data for *a*-Si [2,3] are in conflict with van den Hoven *et al.*'s conclusion but not with their experimental results.

With respect to (2), we refer to work from this laboratory [2–4]. In these studies, *a*-Si samples were prepared by various different techniques comprising conditions similar to those applied by van den Hoven *et al.* These samples were investigated, utilizing the very same Mössbauer state of ^{119}Sn; however, it was populated from the decay of the (ion-implanted) ^{119m}Sn isomer [2]. Irrespective of the type of amorphous material, the same spectrum with only one broadened line was observed, the parameters of which agree very well with those also found by van den Hoven *et al.* for fourfold coordinated Sn. In particular, we point at a Sn Debye temperature of $\Theta = 224(4)$ K for *a*-Si and $\Theta = 226(5)$ K for *c*-Si (Ref. [2]), as compared to $\Theta = 225(10)$ K measured for *a*-Si by van den Hoven *et al.* Indeed, these results substantiate the statement given by van den Hoven *et al.*, "*...that Sn occupies substitutional sites in a-Si,*" whereas the references given in support of this statement (their Refs. [13–16]) are not published (Ref. [16]) or not concerned with *a*-Si (Ref. [13]) or with ion-implanted Sn probes (Refs. [14] and [15]). Clearly, in the context of van den Hoven *et al.*'s study of *ion-implanted* Sb in *a*-Si, the comparison has to be made to *ion-implanted* Sn under similar conditions to make this statement meaningful. It was concluded in Ref. [2] that ion-implanted, isoelectronic Sn probes most likely reflect the genuine amorphous local-structure properties; an association of the Sn probes with point defects in the nearest-neighbor shell was excluded on a $\leq 5\%$ level.

This is in contrast to the behavior in *a*-Si (or *c*-Si) of ion-implanted ^{119}In (Ref. [3]) or ^{119}Sb (Ref. [4]) impurity probes which both decay to the same ^{119}Sn Mössbauer state. Here with both probes, parent-defect complexes occur in the implantation process, which are characteristic for the impurity probe, as concluded from the Mössbauer parameters for the resulting ^{119}Sn daughter complexes. The same impurity-specific complexes are formed in both *a*-Si and *c*-Si. Concerning the Mössbauer parameters of the dominant Sn-vacancy complexes found for Sb implantations, there is once again good agreement between the result from both experiments [1,4], in particular the Sn Debye temperature is lowered to $\Theta = 165(10)$ K. This justifies the conclusion given previously [3] that the same impurity-specific defect structures are formed in the damage cascades in *a*-Si and *c*-Si. However, this does not prove the existence of point defects (vacancies) in impurity-free *a*-Si, i.e., the conclusion drawn by van den Hoven *et al.* Their reasoning for having chosen Sb probe atoms, which are known to trap vacancies in *c*-Si, and thus can be expected to reveal the presence of vacancies also in *a*-Si, is not a sound argument as the same applies to Sn probe atoms. Furthermore, we feel strongly that this type of evidence for the existence of point defects in *a*-Si demands the trapping at the probe atom of, e.g. (mobile) vacancies upon annealing, which were not created in the direct vicinity of the probe atom, i.e., are not created in the implantation process as a local impurity-specific structure due to the presence of the impurity. Analogously, to arrive at conclusions on the possible role of point defects in the relaxation process, a local reordering or annealing induced or influenced by the presence of the impurity has to be excluded as the origin of the occurrence or annealing of impurity-defect complexes.

The ^{119}Sn Mössbauer results for ion-implanted, radioactive In, Sb, and Sn probes give clear evidence that the nature of the local impurity structures found after ion implantation in both *a*-Si and *c*-Si is specific for the impurity. Unfortunately, our ignorance about, e.g., impurity-defect interactions in the damage cascades created by the implantation process prevents conclusions as to whether differences in such reactions are the origin of the differences in the resulting impurity-defect structures. The annealing behavior of the impurity-defect structures upon the structural relaxation of *a*-Si might give a clue as to whether or not point-defect interactions occur. However, the intriguing results obtained by van den Hoven *et al.* for annealed samples, in particular the occurrence of a "missing fraction" with negligible Debye-Waller factor, remain unexplained.

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