DEFECT DYNAMICS IN AMORPHOUS SILICON -- THE RECRYSTALLIZATION PROCESS

SOKRATES T. PANTELIDES
IBM Thomas J. Watson Research Center
Yorktown Heights, New York 10598

ABSTRACT

The mechanism that underlies the recrystallization of amorphous silicon has not been established. It is generally argued, however, that the rearrangement of the network occurs through the breaking of bonds or the introduction of vacancies and that this step is responsible for the observed activation energy (~2.5 eV). It is suggested here that the rearrangement of the network is accomplished through the migration of intrinsic overcoordination defects ("floating bonds") and that this process has a small activation energy (~0.4 eV). The observed large activation energy is actually due to a reaction that inhibits recrystallization. This reaction may be the elimination of preexisting dangling bonds.

INTRODUCTION

It has long been known that amorphized Si layers on crystalline Si substrates recrystallize epitaxially (solid phase epitaxy) with an activation energy of ~2.5 eV.[1] In the early work of Csepregi et al.[1] it was suggested that vacancies may be responsible for the necessary rearrangement of the network. The idea seemed to be supported by beliefs that the formation energy of vacancies in c-Si is about 2.5 eV. It has, however, been established by now by both parameter-free calculations[2] and experiment[3] that the formation energy of vacancies is ~4 eV. In any case, atomistic pictures of how vacancies mediate the recrystallization process have not been advanced. In 1978, Spaepen and Turnbull[4] proposed that the key step in the recrystallization process is the breaking of Si-Si bonds which facilitates the rearrangement of the network. They demonstrated the feasibility of their idea through model drawings of the network in the vicinity of the amorphous-crystalline interface. Germain et al.[5] and Mosley and Paesler[6] later suggested that recrystallization occurs through the diffusion of dangling bonds which arrive at the interface and get captured by other undercoordinated atoms. The resulting further decrease of coordination of these atoms allows them then to "jump" to the crystalline side (see also a paper by Mosley and Paesler in these Proceedings). They recognized however, that the exact nature of the diffusion of dangling bonds, their capture at the interface and the "jump" of atoms from the amorphous to the crystalline side could not be described in detail. In other work, Drosd and Washburn[7] and later Narayan[8] assumed that recrystallization involves diffusion in the amorphous phase and examined the process of adding additional crystalline layers to substrates of various orientations. They did not, however, provide an atomistic description of the diffusion that is necessary in the amorphous phase.

INTRINSIC DEFECTS IN AMORPHOUS SILICON

In the last twenty years, it has been universally believed that the only intrinsic point defect in amorphous Si (a-Si) is the dangling bond or threefold-coordinated Si. Other defects that were occasionally discussed were aggregates of dangling bonds. Overcoordination was generally not discussed at all or was dismissed as impossible. This author[9] recently pointed out that there are in principle two primitive intrinsic point defects in a-Si, namely threefold- and fivefold-coordinated Si atoms, very much like vacancies and self-interstitials are in principle

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the two primitive intrinsic point defects in crystals, and that there are no compelling reasons to dismiss either one. The properties of the fivefold-coordinated Si were investigated and it was concluded that these defects (called also floating bonds because of the nature of the gap-state wave function and by analogy with dangling bonds) are more likely to be the paramagnetic center known as the D center that is commonly identified as a dangling bond. It was further noted that floating bonds can migrate very efficiently, participate in defect reactions, and hence mediate a variety of processes. Many observed phenomena for which atomistic explanations were lacking turned out to be natural and elegant consequences of these reactions. Dangling bonds, on the other hand, cannot migrate as efficiently, largely because of the need to have a microvoid in front of them (by the very definition of a dangling bond, frontside atoms are too far for any appreciable interactions with the dangling bond).

THE KEY STEP FOR RECRYSTALLIZATION

Crystalline Si consists of fourfold-coordinated Si atoms that form six-member rings. Amorphous Si also consists of fourfold-coordinated Si atoms (except for point defects as described above) that form five-, six-, and seven-member rings, perhaps even four- and eight-member rings. It is obvious that the conversion of an amorphous network into a crystalline network requires the conversion of all rings into six-member rings. That's the key step. Earlier workers proposed that this step requires the breaking of Si-Si bonds or the introduction of vacancies.[1,4] We propose here that this step can be accomplished in a natural and elegant way by the migration of preexisting primitive intrinsic point defects. Migration of a floating bond is illustrated schematically in Fig. 1. Note that no particular atom is migrating through the network. Instead, it is the extra bond that is handed over from atom to atom via slight displacements of several atoms. The figure also shows that, after the migration step, the ring on the left increases by one bond whereas the ring on the right decreases by one bond. Thus, migrating floating continually change the size of rings by +1 or -1. When such a migrating floating bond reaches the amorphous-crystalline interface, it will bounce back because it cannot propagate in a crystalline network (isolated floating bonds and isolated dangling bonds cannot exist in a crystalline network). At each such bounce, a five- or seven-member ring is converted into a six-member ring and hence incorporated in the crystalline side.

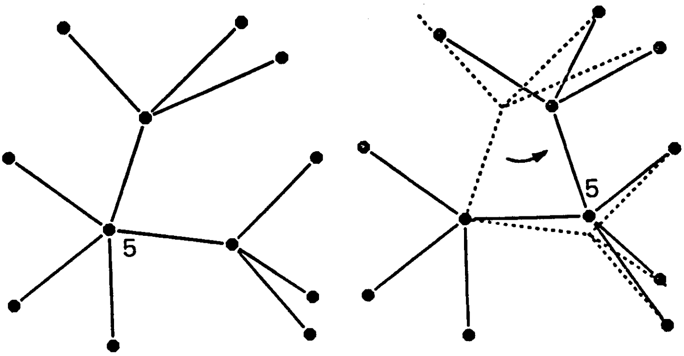

Fig. 1. Schematic illustration of a single step in the migration of a floating bond. From Ref. 9.

In Ref. 9, the properties of migrating floating bonds were examined and the resulting defect reactions were analyzed. By comparing with experimental observations, it was deduced that the migration energy should be small, less than 1 eV. Clearly, therefore, the observed activation energy of recrystallization (~2.5 eV) does not correspond to the energy of the primary step that accomplishes recrystallization. We suggest, therefore, that some other reaction that actually *inhibits* recrystallization is responsible for the observed large activation energy. It is not completely clear at this point what this rate-limiting reaction might be. Dangling bonds may, however, be the culprit. Dangling bonds can also migrate, much the same way floating bonds do by bond switching, changing ring sizes in the process, but the energy required for migration is probably significantly larger.[9] As we noted earlier, the reason is the fact that a true dangling bond by definition has a microvoid associated with it, i.e. atoms on the front side are simply too far to interact with the orbitals of the threefold-coordinated Si atom. For recrystallization to proceed, preexisting dangling bonds need to be dealt with. One way to eliminate dangling bonds is annihilation by floating bonds:

$$\mathrm{FB} + \mathrm{DB} \rightarrow \square ,$$

where FB and DB stand for floating and dangling bond, respectively, and □ stand for a fourfold-coordinated network. There may be kinetic barriers for this reaction, i.e. network constraints that that make floating bonds avoid dangling bonds. Note that the above reaction is the only possible mechanism for annealing either defect in pure a-Si (FB + FB → □ may also occur) and experiments tell us that annealing of the paramagnetic point defects is extremely slow in the absence of hydrogen.[10] Thus, the observed recrystallization activation energy (~2.5 eV) may very well correspond to the dangling bond migration energy. In other words, contrary to earlier suggestions,[1,4-6] dangling bonds do not mediate but actually hinder recrystallization! Floating bonds mediate recrystallization but the motion of the interface is slowed down by the slow-moving dangling bonds. We recognize that no proof is available for such a conclusion. It is a suggestion about the rate-limiting reaction. Other possibilities may exist. Recent work on ion-beam assisted recrystallization, however, seems to support this suggestion. Ion beams enhance recrystallization and reduce the activation energy significantly to only ~0.4 eV,[11] which suggests the following possibility. Ion beams dislodge atoms from their normal positions, creating vacancy-interstitial pairs. Interstitial Si atoms are likely to be highly mobile as they are in crystalline Si where they are known to migrate athermally. These interstitials migrate around until they find a dangling bond with a microvoid. Insertion of the interstitial in the microvoid converts a dangling bonds into several floating bonds which then promptly disperse. Thus, dangling bonds are eliminated without any activation barrier. As a result, recrystallization via migrating floating bonds proceeds unencumbered by dangling bonds. The observed activation energy, ~0.4 eV, corresponds, therefore, to the migration energy of floating bonds.

Another intriguing question is the dependence of the recrystallization velocity on doping. If a-Si contains large concentrations of either donors or acceptors, the recrystallization velocity increases but the activation energy remains unchanged within experimental error. In compensated material (equal concentrations of donors and acceptors), the recrystallization velocity returns to the same value as in undoped material.[1,6] The fact that the activation energy does not change, signifies that the rate-limiting step does not change. That is consistent with the suggestions made above. The increase in the preexponential signifies an increase in the concentration of the point defect mediating the recrystallization. Indeed, it is well-known that the presence of dopants induces an increase in the concentration of D centers.[12] Again, the experimental data are consistent with the suggestions made above. Finally, in compensated samples, the concentration of D centers is the same as in undoped material, leaving the recrystallization velocity unchanged.

CONCLUSIONS

Floating bonds and their migration properties were the subject of earlier papers.[9] The success of that theory in accounting for many observed phenomena that baffled earlier workers provides strong support for the suggestions made in this paper. We simply noted that migration of floating bonds constantly rearranges the network and produces six-member rings, which is the key to recrystallization. No theoretical calculations appear appropriate or are feasible at this stage to strengthen these conclusions. Our second suggestion, namely that dangling bonds actually inhibit and hold up the recrystallization process is far more tentative and speculative. The ion-beam experiments discussed above, seem to support it, however. Thus, the notion deserves further consideration. At this point, it merely provides a possible start in the complex task of unravelling all the details of the recrystallization process. Additional experimental tests of the above ideas would be welcome. We already noted that available experiments favor the notion that the paramagnetic D centers are floating, not dangling bonds. Definitive proof of that, perhaps by ENDOR-detected EPR on ^{29}Si-enriched a-Si, as suggested by Stathis and Pantelides,[13] would be valuable. Then, measurements of the diffusion coefficient of D centers in pure a-Si would test the suggestion that their migration energy is small, ~0.4 eV. Finally, careful monitoring of EPR and luminescence signals in different samples would test whether dangling bonds are indeed nonmagnetic and have a luminescence line at ~0.9 eV, as suggested in Ref. 9. If so, the dangling bond diffusion coefficient would be measurable by profiling of the ~0.9 luminescence peak. Thus, determination of the dangling and floating bond migration energies are in principle possible and would provide fairly definitive tests of the ideas expounded in this paper.

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