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RAPID PHASE TRANSITIONS IN SILICON UNDER PULSED-LASER IRRADIATION

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ABSTRACT

Different pulsed laser induced phase transformations in silicon are discussed and compared, with emphasis on random and epitaxial explosive crystallization of ion-implanted amorphous Si and on formation of amorphous Si from the melt.

I. INTRODUCTION

Rapid phase transitions in Si induced by pulsed-laser irradiation have been studied for almost 15 years now. In the early years of research on this subject there was a lively scientific discussion concerning the nature of the phase transformations involved. The question was roughly whether they are purely thermal in nature or influenced by the laser-generated electrons and holes. The present opinion is that most processes can be described well by simple thermal models, although there are indications that in a limited number of cases non-thermal effects may play a role (see for a review reference [1]). Nevertheless laser-induced phase transformations are still a subject of fundamental interest. The use of nano- or picosecond laser irradiation offers the possibility to study melting and solidification as well as solid-phase crystallization under conditions far from thermodynamic equilibrium. As yet there are no theories available to predict the behaviour of Si under these circumstances in an accurate way. This is both true for nucleation and for growth of phases.

In this contribution we will discuss different pulsed laser induced phase transformations in ion-implanted amorphized Si and single-crystal Si, leading to the formation of single-crystal Si (c-Si), large-grain polycrystalline Si (lgp-Si), fine-grain polycrystalline Si (fgp-Si) or amorphous Si (a-Si).

- First, epitaxial regrowth from the melt. This process can be used to remove ion-implantation damage in c-Si (pulsed-laser annealing). By complete melting of the damaged or amorphized region and subsequent solidification from c-Si substrate seed, it is possible to obtain c-Si without extended defects [2].
- Second, formation of a-Si from the melt. Liquid Si (l-Si) may solidify into a-Si at high velocities and/or large undercooling [3] or at low velocities when a seed for crystal growth is absent [4].
- Third, random explosive crystallization (EC) of a-Si. It is well-known that a-Si may be transformed into fgp-Si via a self-propagating process of melting and solidification [5-14]. Besides fgp-Si, usually a surface layer of lgp-Si is formed.
- Finally, epitaxial EC of a-Si. Recently, Polman and coworkers studied this process, which can be initiated in buried a-Si layers formed by high-energy ion implantation and which yields single-crystal Si [15-20].

The results from these different experiments will be compared and used to address the issues of ultra-rapid solidification and nucleation in Si.

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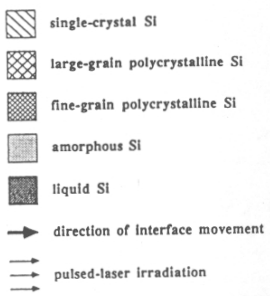
II. EPITAXIAL REGROWTH FROM THE MELT

The first use of pulsed lasers in silicon processing was by Russian researchers for annealing of ion implantation damage [21]. For this purpose one generally uses nanosecond pulses from ruby lasers, Nd:YAG lasers or, more recently, excimer lasers. By irradiation at an energy density in the order of 1 J/cm^2 a damaged or amorphized surface layer of up to 1 μm thickness can be melted. If the melt thickness is sufficiently large, subsequent epitaxial crystal growth starts from the undamaged c-Si substrate and the resulting material is basically defect-free [2]. Typical regrowth velocities are several m/s. A schematic of this process is given in Fig.1. The process appears relatively simple but has been studied in detail because it offers a potential alternative to furnace annealing of implantation damage. In addition, it has been used to test various thermal models and their parameters to describe laser-induced melting and solidification [22,23].

LEGEND FIGURES 1-5



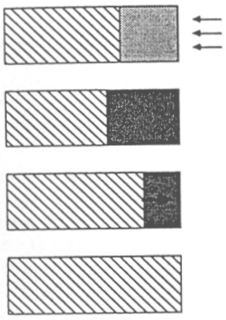


FIGURE 1. Pulsed-laser annealing of ion-implantation damage

III. AMORPHOUS REGROWTH FROM THE MELT

The situation described in the previous section becomes more complicated when the regrowth velocities exceed ≈10 m/s. This can be achieved for shallow melting of c-Si, by using picosecond pulses or UV pulses of < 10 ns [3,24-27]. It has been found that epitaxial regrowth breaks up to amorphous regrowth at interface velocities of ≈10-15 m/s, dependent on the orientation of the crystal [3], see Fig.2. Breakdown occurs at relatively low velocities for Si(111) and at high velocities for Si(100). It has been attributed to the fact that at high velocities the atomic rearrangements at the interface are too slow to permit (perfect) crystal growth. This results in defect formation and multiplication and ultimately in amorphous phase formation. We note that this kinetic arguement is not the only possible explanation for the occurrence of a maximum crystal growth velocity. This will be discussed in detail in section V.

a-Si can only be formed when the interface temperature is below the melting temperature of a-Si (T_{ma}), being approximately 200-250 K below that of c-Si (T_{mc}) [5,28]. Measurements of the velocity *vs.* undercooling relationship in the temperature range around T_{mc} (1685 K) indicate that an undercooling of ≈90 K is required to obtain an interface velocity of 6 m/s, or 15 K/(m/s) [28]. Extrapolation to larger undercooling then yields an undercooling of 15 m/s • 15 K/(m/s) = 225 K around the velocity at which a-Si forms (in case of melting of

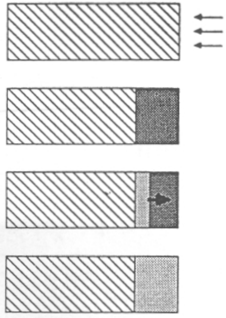


FIGURE 2. Formation of a-Si from the melt: fast growth.

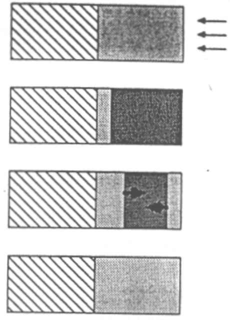


FIGURE 3. Formation of a-Si from the melt: slow growth.

Si(100)). This number appears to coincide with the estimated value of T_{ma}. In section V, however, we will show that this may be a misleading coincidence.

Another way to form a-Si from the melt is by melting ion-implanted a-Si using short (<10 ns) pulses from a frequency-doubled Nd:YAG laser or a ruby laser. When the a-Si layer is not fully melted, there is no seed for crystallization and amorphous regrowth is found to occur both from the back a-Si/l-Si interface and from the surface [4,29] (see Fig. 3). The velocity at which a-Si is formed under these conditions is only 1-3 m/s, which is much lower than the velocity of ≈15 m/s required to induce break-up of crystal growth. It has been argued that amorphous regrowth upon melting of a-Si has never been observed in pure a-Si and hence is an impurity-related process [30]. This statement is not in agreement with observations on Si-implanted a-Si [31]. Amorphous regrowth, however, is often found to evolve into EC [32], which may complicate its observation.

IV. RANDOM EXPLOSIVE CRYSTALLIZATION

Since the pioneering experiments by Takamori et al. [33] and Matsuda et al. [34] it is well-known that a-Ge and a-Si can be crystallized in a spontaneous way by applying a localized energy pulse. Once crystallization has been started, it is driven further by the latent heat effectively released upon transformation from the amorphous to the crystalline phase. It has been shown that in most, if not all, cases the transformation is mediated by melting of the amorphous phase [20]. Most experiments have been carried out on pulsed laser induced EC of ion-implanted a-Si [5-14]. This system is well-defined and very suitable for detailed micro-structural and time-resolved analysis. The general picture that has evolved is given in Fig.4. Upon irradiation with a low-energy laser pulse (pulselength typically >20 ns), a thin surface layer of a-Si is melted. This melt is highly undercooled with respect to the crystalline phase and will therefore tend to crystallize. Since no seed for crystallization is present, the material formed is polycrystalline (lgp-Si). The latent heat released upon this crystallization is sufficient to heat and melt underlying a-Si and hence a secondary, highly undercooled buried layer of l-Si is formed. This melt also crystallizes under the release of latent heat and causes further melting. In this way a self-sustained process of melting and crystallization is initiated. A thin buried layer of l-Si runs into the a-Si at a velocity of 8-15 m/s [5,9,10,12], transforming amorphous material into randomly-oriented fgp-Si. It is noted that this picture is somewhat simplified [12,14], but it is nevertheless very useful to discuss the basic processes involved.

The most difficult part in random EC is to understand and describe nucleation of the crystalline phase. This problem is discussed in detail in Ref. [20] and we will only address it briefly here. As far as formation of fgp-Si is concerned, it is essential to know where and when the nuclei are formed which eventually grow out to crystallites of 5-10 nm. At present it is not even clear whether they are formed in the a-Si in front of the buried l-Si layer [35], at the a-Si/l-Si interface [36] or in the l-Si layer itself [37] (although recent experiments [38] have shown that nucleation rates in l-Si are much too small to support the latter model). The nucleation leading to lgp-Si formation is not well understood either. Basically the same questions hold as for formation of fgp-Si, but a difference is the velocity at which the a-Si/l-Si interface moves into the a-Si, which is low (especially around the turning point of the surface melt) [39] in comparison to the 8-15 m/s found for fgp-Si formation.

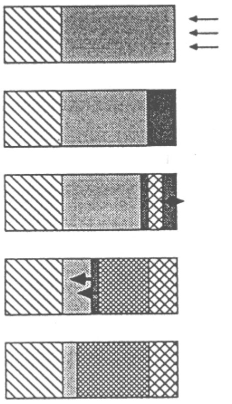


FIGURE 4. Random explosive crystallization of a-Si.

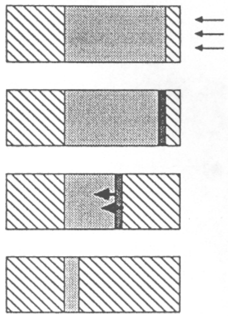


FIGURE 5. Epitaxial explosive crystallization of a-Si.

V. EPITAXIAL EXPLOSIVE CRYSTALLIZATION

Recently, Polman and coworkers have investigated pulsed laser induced EC of a-Si layers buried beneath a c-Si surface layer [15-20]. These structures can be prepared by high-energy ion implantation into c-Si. Since the c-Si top layer has a lower optical absorption coefficient and a higher melting temperature than the a-Si layer underneath, it is possible to irradiate and heat a-Si through the c-Si, which results in buried melting of a-Si at the a-Si/c-Si interface. This melt is highly undercooled with respect to the adjacent c-Si and immediately crystallizes with the c-Si as a seed. The latent heat released upon crystallization is sufficient to heat and melt underlying a-Si, which will also crystallize. In this way a self-sustained process is triggered, which is similar to that in a-Si surface layers. The major difference is that in this case the material formed is single-crystal, epitaxially aligned with the c-Si on top (see Fig.5).

It has been found that the c-Si formed by epitaxial EC contains twins, but is free of polycrystallites. This is remarkable, since the overall features of this type of EC are similar to those of random EC. Apparently the nucleation and growth mechanism leading to fgp-Si formation is suppressed under the conditions of epitaxial EC (see Ref. [20] for a discussion).

The velocity of epitaxial EC has been measured to be 15-16 m/s for Si(100) [15,16,19]. In contrast to the velocity of the l-Si layer in random EC, the velocity in epitaxial EC remains constant during propagation through the a-Si (over ≈350 nm), as was concluded from time-resolved optical reflectivity measurements. The temperature of the freezing l-Si/c-Si interface, on the other hand, is calculated to make an excursion over ≈70 K. Immediately after melting of the a-Si, the temperature at the l-Si/c-Si interface is approximately equal to T_{ma} (≈1460 K [5]). Due to the release of latent heat upon crystallization and to additional heating by the tail of the laser pulse the temperature at this interface rises. Note that the temperature at the a-Si/l-Si melt front is assumed to remain close to T_{ma}. After reaching a maximum of ≈1530 K it decreases again due to heat conduction into the c-Si substrate. Eventually the temperature of the melting and freezing interfaces drops below T_{ma} and EC is quenched. From the measured crystallization velocity and the corresponding calculated temperatures, it is possible to construct a part of the velocity *vs.* undercooling relationship in a temperature regime which is very difficult to explore in other experiments (≈155-205 K undercooling). It is found that the crystallization velocity saturates at 15-16 m/s for this large undercooling, in qualitative agreement with predictions [40,41]. Various models for crystal growth, however, differ considerably in their basic assumptions. Best agreement between theory and experiment is found for models in which diffusive motion in l-Si at the interface is the rate limiting factor [19,40,41].

An interesting consequence of the experiments described just before is that the crystallization velocity can never exceed 15-16 m/s, which coincides with the observed threshold velocity for break-up of crystal growth into amorphous growth (see section III). This implies that break-up is not necessarily related to the velocity of the interface (which is constant in the temperature regime of interest) as has been assumed, but may also be related to the degree of undercooling below T_{ma}. The observation of a plateau in the undercooling *vs.* velocity relationship shows that an extrapolation to large undercooling of data obtained at small undercooling is not a useful thing to do. The coincidence of T_{mc}-T_{ma} ≈ 225 K and the extrapolation 15 m/s • 15 K/(m/s) = 225 K (see section III) may just be good (or bad) luck. Note that the value of 15 K/(m/s) is not accurately known [42].

VI. CONCLUSIONS

We have discussed and compared different pulsed laser induced rapid phase transformations in silicon. As a result of intensive investigations, understanding of these processes has steadily improved over the past decade. Most processes can now be described well in phenomenological way. Important remaining questions to be solved mainly concern the fundamental mechanisms underlying the phase transformations, particularly random nucleation of the crystalline phase and solidification at very high (>10 m/s) velocities.

VII. ACKNOWLEDGEMENTS

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