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 accurrate 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 amorphous Si and single-crystal Si, leading to the formation of single-crystal Si (c-Si), large-grain polycrystalline Si (LPS), fine-grain polycrystalline Si (fgp-Si) or amorphous Si (a-Si).

1. 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].

2. Second, formation of a-Si from the melt. Liquefied Si (LPS) 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].

3. Third, random explosive crystallization (REC) 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 LPS-Si is formed.

4. Finally, epitaxial REC 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/cm² 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 e-Si substrate and the resulting material is basically defect-free [2]. Typical regrowth velocities are several μm/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].

III. AMORPHOUS REGROWTH FROM THE MELT

The situation described in the previous section becomes more complicated when the regrowth velocities exceed ~10 μm/s. This can be achieved for shallow melting of a-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 μm/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 formations and multiplication and ultimately in amorphous phase formation. We note that this kinetic argument 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_m), being approximately 200-250 K below that of e-Si (T_m) [3,28]. Measurements of the velocity vs. undercooling relationship in the temperature range around T_m (1685 K) indicate that an undercooling of ~80 K is required to obtain an interface velocity of 6 μm/s or 15 K/off (28). Experiments on larger undercooling then yields an undercooling of 15 μm/s or 15 K/off = 223 K around the velocity at which a-Si forms (in case of melting of

S(100). This number appears to coincide with the estimated value of T_m. 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 need for crystallization and amorphous regrowth is found to occur both from the back a-Si/e-Si interface and from the surface [4,29] (see Fig. 2). The velocity at which a-Si is formed under these conditions is only 1-3 μm/s, which is much lower than the velocity of ~15 μm/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 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 Takenori 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 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 [3-14]. This system is well-defined and very suitable for detailed microstructural and time-resolved analysis. The general picture that has evolved is given in Fig. 4. Upon irradiation with a low-energy laser pulse (pulsedwidth 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 need to crystallize. Since no seed for crystallization is present, the material formed is polycrystalline (polycrystalline-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 a-Si is formed. This melt also crystallizes under the release of latent heat and causes further melting.
It has been found that the c-Si formed by epilaxial EC contains twins, but is free of polyocrystallites. 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 fgr-Si formation is suppressed under the conditions of epilaxial EC (see Ref. [20] for a discussion).

The velocity of epilaxial EC has been measured to be 15-16 m/s for Si(100) [15,16,19]. In contrast to the velocity of the s-Si layer in random EC, the velocity in epilaxial EC remains constant during propagation through the a-Si layer (20-25 m/s), as was concluded from time-resolved optical reflectivity measurements. The temperature of the s-Si/a-Si/Si interface, on the other hand, is equal to the maximum of the laser pulse. Due to the slower rate of phase transition and diffusion at the interface, the layer temperature is higher by 100-150°C than at the laser pulse peak. Thus the a-Si/a-Si/Si interface is rapidly annealed and the laser pulse is effectively absorbed in the a-Si/a-Si/Si interface. At a maximum of 1500 K it decreases again due to heat conduction into the a-Si substrate. Eventually the temperature of the material and freezing interfaces drops below 1450 K (200°C) and the growth process is quenched.

V. EPILAXIAL EXPLOSIVE CRYSTALLIZATION

Recently, Poelman and coworkers have investigated pulsed laser induced EC of a-Si layers buried beneath a c-Si surface layer [20-26]. These structures can be prepared by high-energy ion implantation into c-Si. Since the a-Si layer has a lower optical absorption coefficient and a higher melting temperature than the c-Si layer underneath, it is possible to irradiate and heat the a-Si layer through the c-Si, which results in 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 latter 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, epilaxially aligned with the c-Si on top (see Fig. 5).

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. Many 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.

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VIII. REFERENCES