

# Multiinterface Solar Cell with Active Substructure Buried in Single-Crystal Si by Implantation Processing<sup>+</sup>

Z.T. KUŹNICKI,<sup>1\*</sup> J. THIBAUT,<sup>2</sup> F. CHAUTAIN-MATHYS,<sup>2</sup> S. DE UNAMUNO<sup>1</sup>

<sup>1</sup> CNRS, Laboratoire PHASE (UPR 292), Strasbourg, France

<sup>2</sup> CEA/Dep. Recherche Fondamentale sur la Matière Condensée, Grenoble, France

*Local modification of single-crystal silicon can consist of a planar nanostructure buried at a given depth (e.g. tens of nanometers). This substructure can take the form of a thin amorphized layer having two a-Si/c-Si heterointerfaces at its edges. The morphology of the interfaces and the structural homogeneity of the substructures represent the main factors for device performance improvements on the mesoscopic scale.*

*The first stage of the local single-crystal Si modification consists of a post-implantation structural unification of the transition zones. The two Si phases at each heterointerface become homogeneous each with its own bulk. They are separated by a very thin transition zone. This is the basic process for fabrication of the new so-called d-BSF solar cells. High resolution electron microscopy shows that a thermal treatment is able to transform totally the structural mismatch between single-crystal and amorphized phases into well-defined zones, each conserving its structural characteristics on the atomic scale. This signifies in practice that structural transition zones can be completely removed to leave sharp heterointerfaces in their place. The processes described in this paper represent a basis for defect and stress engineering of Si solar cells.*

## 1. Introduction

The idea of a superposition of different materials by heteroepitaxy can be extended to a conjugation of different phases (of the same or of different materials) [1]. This approach allows for: (i) widening of material modification possibilities, (ii) new material combinations and (iii) new device arrangements [2-5]. However, in most cases of heteroepitaxy, a single-crystal superposition (or single-crystal and amorphous superposition) involves a lattice mismatch at the interface between different materials. This will entail a high recombination velocity, which has to be controlled with specially adapted thin intermediate layers [5, 6].

Even with a very small density of defects at the

heterointerface between a single-crystal and an amorphous phase a stress in the initial and deposited layers will be produced, which can be spread within the heterointerface transition zone [7]. We have observed stress effects in an amorphized Si (a-Si) single-crystal Si (c-Si) superposition produced by implantation-buried amorphization conjugated with subsequent thermal treatment [8]. Our experience opened the way to new potentially useful structures [9]. After an adequate thermal treatment, the two Si phases at each heterointerface become homogeneous each with its own bulk. They are separated by a very thin structural transition zone on the atomic scale. This two Si phase superposition has been observed for the first time as being free from detrimental interface states.

\* corresponding author: Zbigniew T. Kuźnicki, CNRS, Laboratoire PHASE (UPR 292), BP 20, 23 rue du Loess, 67-037 Strasbourg, CEDEX 2, France, phone: +33-388106251 fax: +33-388106293, e-mail: KUZNICKI@phase.c-strasbourg.fr

<sup>+</sup> Presented at the 12<sup>th</sup> School of Optoelectronics: Photovoltaics – Solar Cells and Infrared Detectors, Kazimierz Dolny, May 22-24, 1997.

Since flat buried layers with low defect concentration are desired for most technological applications, controlling when and how stress activity occurs becomes a key issue in material superposition [10]. Because of numerous post-implantation defects with different behaviors, the as-implanted structures cannot be used without a conjugated treatment. An adequate treatment has to take into account several stages differentiated from each other by defect gettering or defect modification. This paper describes a-Si/c-Si transition zone modifications during regrowth and annealing which are vital to improvements in Si optoelectronic performance. This is the basic process for fabrication of the new so-called d-BSF solar cells. ("d" signifies the thin inserted substructure and "BSF", back surface field).

## 2. Technology

High efficiency solar cells have to exploit the largest possible range of the solar spectrum, i.e. IR photons for the sub-gap range and the additional energy of energetic photons from the UV and the visible ranges. The superposition of different materials is an important subject of materials engineering because of its applicability to a variety of technological situations [1]. One area presently attracting a good deal of research is the superposition of electronic and optoelectronic materials by way of active substructures [2]. By adding active interfaces, it is possible to tailor the electronic or optical (or both) properties in a way which is just not possible with simple modifications or superposition of different materials [3].

The two above mentioned Si phases seem to be very interesting for optoelectronics from this point of view because of their complementary optical and electronic properties [8, 4-6]. The usefulness of a different phase superposition is determined by the atomic-like order at the heterointerface (rather than at the heterointerface transition zone). The atomic order of single-crystal material is well defined. In amorphous Si this order is characterized by short-range interactions of a given type [11], depending on the material origin of CVD, plasma deposition or implantation. To distinguish the disordered Si structure obtained by ion beam implantation we call it amorphized (not amorphous) Si material as in [11].

In experimental samples the absorbing substructures (buried planar continuous 50-70 nanometers thick layers) have been made by P ion implantation in the (100) oriented Si single-crystal at  $\approx 180$  keV at room temperature [3, 12]. The implantation dose has been

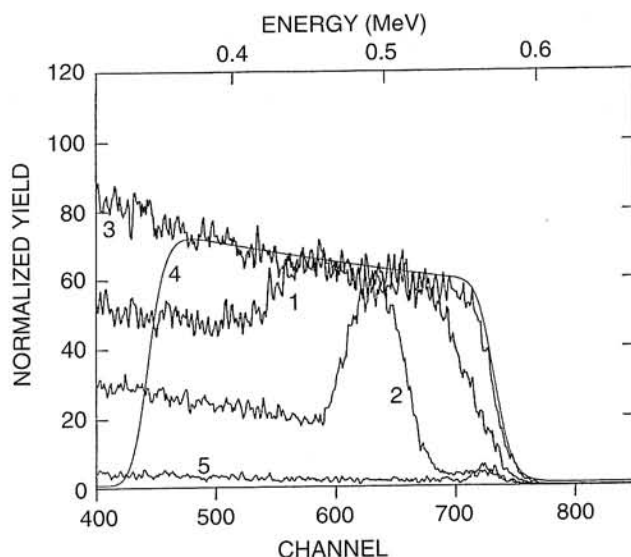


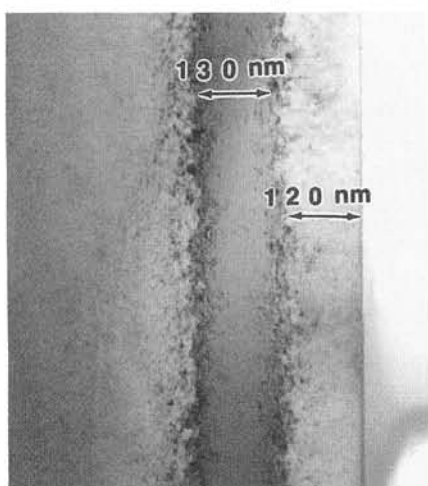
Fig. 1. RBS characterization of a P implanted heterointerface emitter [12]: curve (1) – distribution for the as-implanted multiinterface structure; curve (2) – final structure after thermal treatment; curve (3) – reference distribution for amorphous Si; curve (4) – a simulated RBS distribution for an amorphous Si layer; and curve (5) – reference distribution of single-crystal Si. The amorphized substructure has a thickness of  $d \approx 70$  nm at the depth  $x\Delta \approx 100$  nm. The P-N interface is inserted at a depth  $x_j \approx 500$  nm from the front face.

adapted to produce a sufficiently thick buried amorphization and a limited defect density in the single-crystal layers. The doses varied between  $5 \times 10^{14}$  and  $10^{15}$  cm $^{-2}$ . After a subsequent thermal treatment at 500°C [10, 12] during 15 to 30 min (the precise conditions were defined in a separate comparative study [3]), the 50-70 nm thick amorphized layer was situated below a single-crystal layer of 100 nm. In Figs. 1 and 2 the modification under thermal treatment is visualized (the Figs. 1 and 2 concern different samples). The modified material has a large concentration of implanted dopants which are in practice totally ionized [13]. The electrically neutral impurities occur only in the deeper single-crystal region under the substructure.

Fig. 1 shows the comparison of a heterointerface emitter of the d-BSF cell before and after thermal treatment as obtained by Rutherford Backscattering Spectroscopy (RBS) under channeling incidence with 2 MeV 4He. The amorphized and single-crystal regions can be distinguished by the amorphous and single-crystal reference signatures [10, 12]. A shift of each (upper and lower) of the a-Si/c-Si heterointerfaces during annealing can be observed. The bottom interface moves more rapidly than the upper one [14].

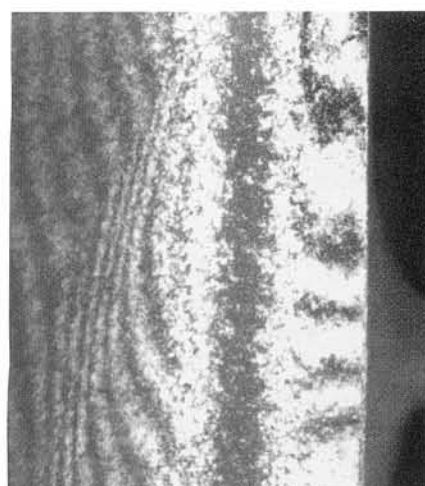
The results presented in Fig. 1 are confirmed by the High Resolution Electron Microscopy (HREM) im-

Lower interface      Upper interface

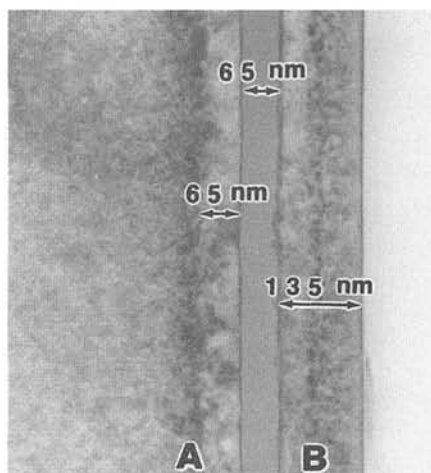


a) Light background before thermal treatment

Lower interface      Upper interface



Dark background before thermal treatment



b) Light background after thermal treatment



Note: this photo has not the same magnification

Dark background after thermal treatment

Fig. 2. HREM images of the buried amorphized substructure formed by impurity implantation [15]: a) as-implanted, b) after adequate thermal treatment. The geometrical dimensions are visualized in the figure.

ages (Fig. 2 [15]). In this case HREM allows another important observation. The buried amorphized substructure contains a lot of single-crystal inclusions within its bulk before the annealing. The a-Si/c-Si as-implanted transition zones are formed of a mismatch of single-crystal and amorphized "grains" which cannot in any case be ascribed as a flat interface. After an adequate thermal treatment, the epitaxial regrowth [16] (also called solid phase epitaxy) of the amorphized Si leads to a transformation characterized by the following: (i) a reduction of the buried layer thickness, (ii) a total homogenation of the amorphized material (Fig. 3

illustrates the effect of the post-annealing homogenation of the amorphized phase) and (iii) the smoothing out of a-Si/c-Si interfaces corresponding to practically total disappearance of structural transition zones. A multiinterface flat nanostructure (with a buried amorphized layer) with a large area has thus been formed by P impurity implantation and a conjugated thermal treatment. The initial poor quality transition zones changed their structural aspects completely during the suitable thermal treatment. The next step concerns a fine characterization of the transition zone structure and its modifications during annealing.

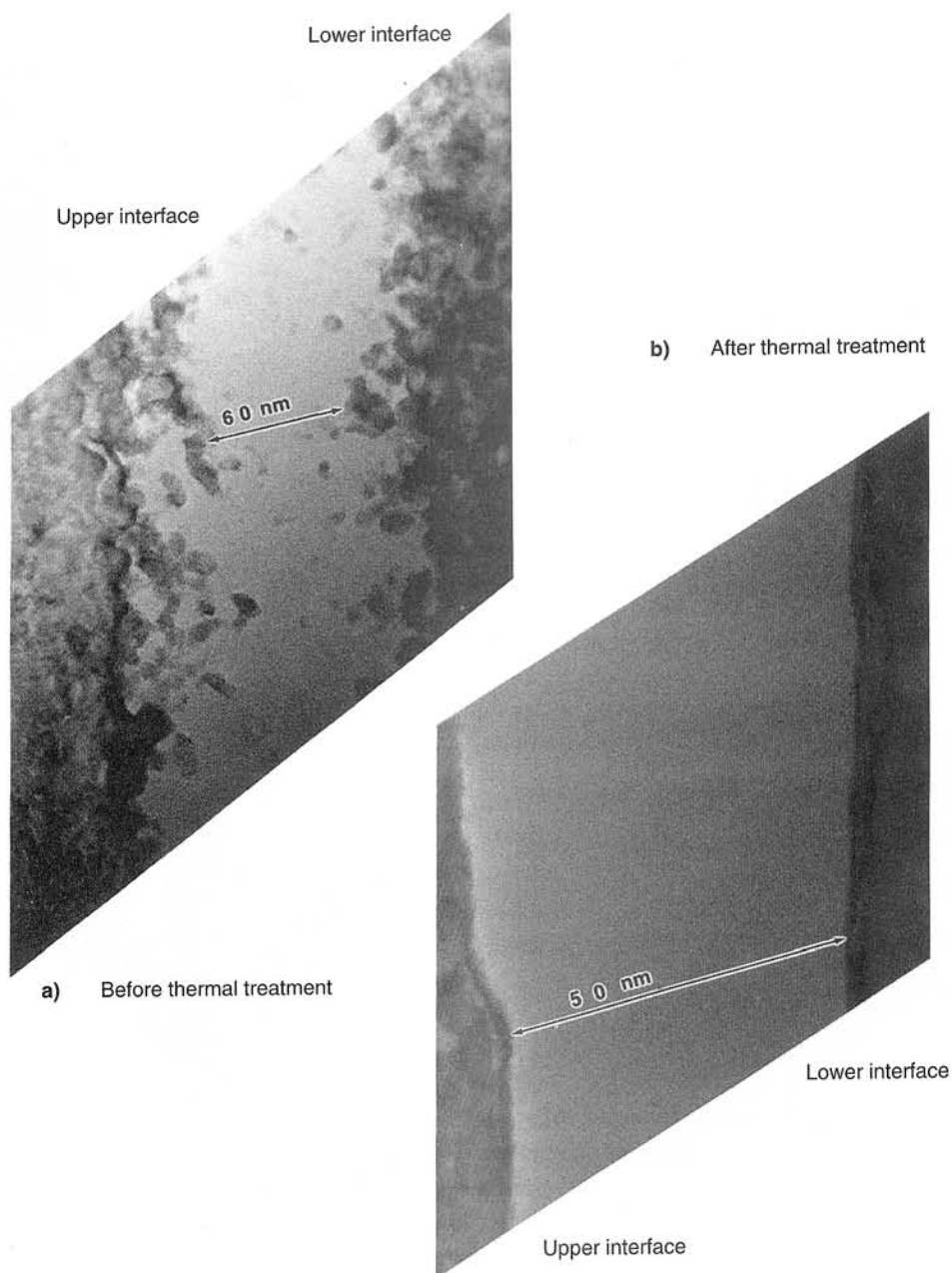


Fig. 3. HREM images from Fig. 2 at greater magnification [15]: a) as-implanted, b) after adequate thermal treatment. The effect of the post-annealing homogenization of the amorphized phase is well-illustrated.

### 3. Characterization of the d-BSF solar cell structure

An active interface can be defined as a mesoscopic-scale device component which is able to complete or even dominate the basic material properties. The transformation of a multilayer to a multiinterface structure can cause considerable modification of device properties without any conspicuous material modification. This fundamental effect has been revealed on the structural level by HREM images of as-implanted and an-

nealed structures. Optoelectronic improvements of the single-crystal Si solar cell are controlled by the atomic scale structural behavior of the a-Si/c-Si heterointerface.

#### 3.1. As-implanted transition zone

The rough heterointerface transition zone of an as-implanted multilayer device is composed of a mismatched superposition of the single-crystal and amorphized cluster-like "grains." The single-crystal and



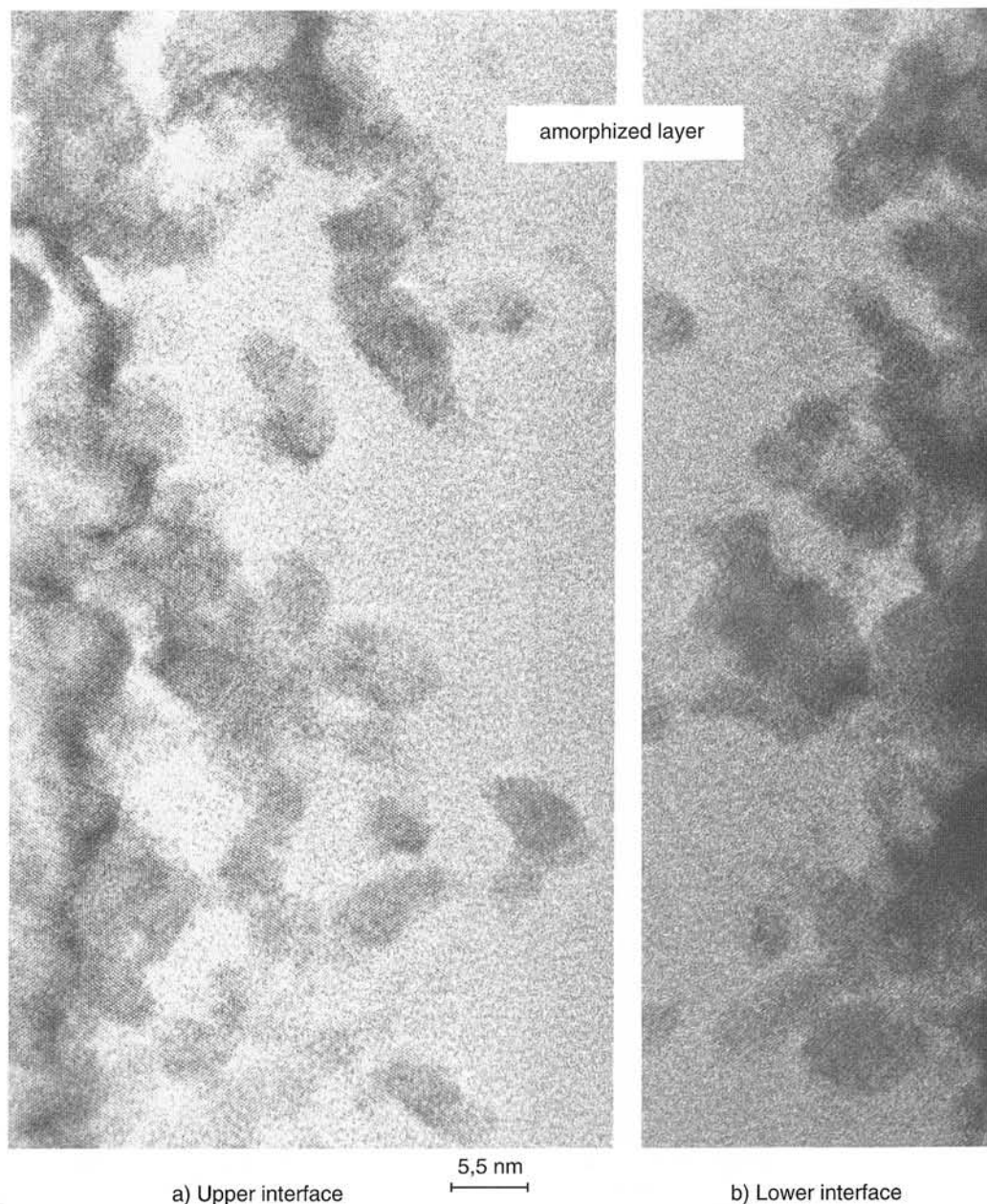


Fig. 4. HREM images from Fig. 3 at greater magnification [15]. The two as-implanted transition zones, upper (a) and lower (b), are visualized on the atomic scale.

amorphized grains can contain hundreds of atoms. The non-annealed transition zone is relatively wide (2.5-50 nm) and its composition changes gradually from a totally single-crystal material to a totally amorphized material. Some single-crystal inclusions within the amorphized bulk are also present. Fig. 4 shows the as-implanted transition zones of the upper and lower interfaces.

### 3.2. Annealed transition zone

After an adequate thermal treatment, both the upper and lower structural transition zones practically disap-

pear (Fig. 3). The thermal treatment causes a dilution of the included single-crystal clusters which seem to be too small for germination of a polycrystalline structure (their initial crystalline orientation is conserved after amorphization). The single-crystal outside the amorphized layer allows regrowth of the former crystalline lattice. These phenomena allow the strong homogenization of the buried layer. The structural transition zone disappears and a flat heterointerface is formed. In Fig. 5 the effects of the considerable transformation of the annealed transition zones can be observed. The transition from the single-crystal to the amorphized material phase is realizable on a one atomic layer scale.

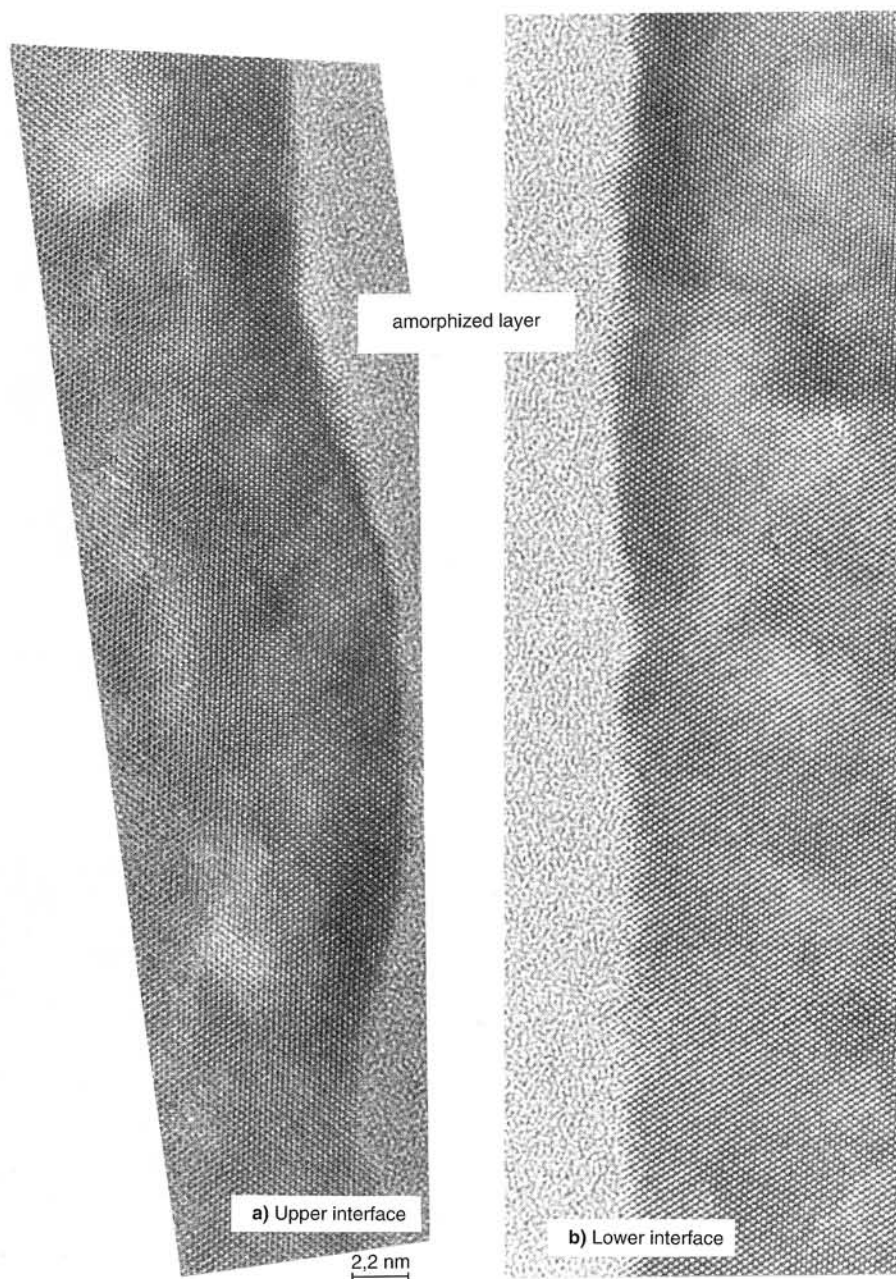


Fig. 5. HREM images from Fig. 3 at greater magnification [15]. The two annealed transition zones, upper (a) and lower (b), are visualized on the atomic scale. An active interface is well-formed at the upper as well as at the bottom substructure edges. After annealing, the built-in stress field inserted within the a-Si/c-Si transition zone exhibits a perfectly two-dimensional behavior.

The present approach consists in producing a multi-interface structure from initial multilayer superposition of the two Si phases which are complementary from the optoelectronic point of view. It seems that the active interface free of extended defects allows control of the optoelectronic properties of the transition zone. Because the quality of the a-Si/c-Si heterointerface dominates the device behavior, it will be possible in this way to realize in practice the new concept of the d-BSF solar cell of very high efficiency.

## 4. Discussion

We have tried to indicate that the effect of stress activity [7] can be controlled in a way that minimizes its negative aspects (or better, exploits its positive aspects) on the device level. In the a-Si/c-Si transition zone, there are two of local stresses because of the amorphized and single-crystal density difference (of  $\approx 2\%$ ): local stress existing at heterointerfaces between single-crystal and amorphized material with separated grains

(amorphized or single-crystal) and local stress along the smoothed-out heterointerface [7]. Possible relaxations can appear on both the atomic and the mesoscopic scales.

Because the small "grains" correspond to a very limited quantity of material, their three-dimensional stress behavior depends on the grain size. With small amorphized grains, an additional local compression which cannot be relaxed in any direction is present. This stress can cause a different atomic arrangement [11] and a corresponding local three-dimensional deformation. The mesoscopic relaxation along the flat heterointerface shows a uni-axial behavior and appears in the direction perpendicular to the device surface.

Stress-induced shape changes of the transition zone influence the interface morphology only during the early stages of the recrystallization. It seems that the buried amorphized material forms a compressively stressed layer after annealing. During the post-implantation annealing, the mean heterointerface stress changes from three- to two-dimensional [9]. At the as-implanted single-crystal edge of the transition zone, it is a three-dimensional stress of small amorphized grains and at the amorphized edge it is a two-dimensional stress of the uni-axially-relaxed amorphized layer. The post-annealing sharpening of the transition zone leads to a further enhancement and homogenization of local stress. This type of stress concentration should lead to misfit-dislocation source behaviour by lowering the barrier to dislocation nucleation in a single-crystal lattice. In an amorphized material, the same effect can lead to a new atomic arrangement which signifies a new defect behavior.

High resolution electron microscopy visualizes the basic structural transformations of the a-Si/c-Si transition zone found earlier by other techniques. The as-implanted heterointerfaces are rough. After a thermal treatment the interfaces become flat on the atomic scale. But the velocity of the solid phase epitaxy is much greater for the deeper interface than for the shallower. The amorphized layer becomes homogeneous because of the "dilution" of small single-crystal inclusions. It has been observed that the upper (and lower) single-crystal layer, damaged during the implantation, can be gettered and homogenized by adequate annealing up to the a-Si/c-Si heterointerface.

The short-range atomic order at the heterointerface transition zone in the multiinterface design is higher than in the case of corresponding heterojunction design. So the final atomic order desired for a multi-interface solar cell at an a-Si/c-Si heterointerface conjugated with a useful local stress can be obtained by

implantation. To reduce, modify and control the post-implantation defects, an adequate thermal treatment is necessary. Stress relaxation in nanostructural mismatched heterointerface systems has become a matter of great urgency with regard to possible applications of stressed nanolayers in optoelectronic systems and, in particular, in high efficiency Si solar cells. It is clear that ion beam processing allows the formation of all of the basic d-BSF device components. The final solar cell structure can be much better controlled on the heterointerface transition zone level in the multiinterface design than in the case of corresponding heterojunction design. So the final PV conversion efficiency can be greater than those of heterojunction cells, with 21% being obtained up to now [5].

## Acknowledgements

The authors wish to express their thanks to J.-J. Grob and Y. Le Gall of the Laboratoire PHASE of Strasbourg for their experimental aid.

## References

1. Y.S.Tsuo, X. Wu, J.L. Alleman, X. Li, Y. Qu, T.F. Cizek, R.E. Hollinsworth, and P.K. Bhat, 23th IEEE PVSC, Louisville, USA, 10-14 May 1993, p. 281.
2. Z.T. Kuźnicki, *J. Appl. Phys.*, **74** (1993) 2058.
3. Z.T. Kuźnicki, J.-J. Grob, and J.-C. Muller, H.E. Strażynska-Kuźnicka, French Patent No 94 08885 of 13 July 1994.
4. M. Tanaka, M. Toguchi, T. Matsuyama, T. Sawada, S. Tsuda, S. Nakano, H. Hanafusa, and Y. Kuwano, *Jpn. J. Appl. Phys.* **31** (1992) 3518.
5. T. Sawada, N. Terada, S. Tsuge, T. Baba, T. Takahama, K. Wakisaka, S. Tsuda, and S. Nakano, 1st World Conference on Photovoltaic Energy Conversion (WCPEC), Hawaii, USA, 5-9 December 1994, p.1219.
6. D. Della Sala, F.Roca, G. Fameli, P. Grillo, F. Pascarella, and F. Ferrazza, 12th E.C. PVSEC, Amsterdam, the Netherlands, 11-15 April 1995, p. 799.
7. S. Milita, and M. Servidori, *J. Appl. Phys.* **79** (1996) 8278.
8. J.R. Dennis, and E.B. Hale, *J. Appl. Phys.* **49** (1978) 1119.
9. Z.T. Kuźnicki, 1995 MRS Fall Meeting, November 27 – December 1, Boston, USA.
10. Z.T. Kuźnicki, J.-J. Grob, and B. Prévot, E-MRS Spring Meeting, Strasbourg, France, 22-26 May

*Multiinterface solar cell with ...*

- 1995, published in Nucl. Instr. and Meth. in Phys. Res. B, 112 (1996)188.
11. T. Motooka, Thin Solid Films **272** (1996)235.
  12. Z.T. Kuźnicki, J.-J. Grob, and L. Wu, Appl. Phys. Lett. **67** (1995)3798.
  13. Z.T. Kuźnicki, L. Wu, J.-J. Grob, and L. Ventura, 12th E.C. PVSEC, Amsterdam, the Netherlands, 11-15 April 1994, p. 1056.
  14. L. Csepregi, E.F. Kennedy, T.J. Gallagher, J.W. Mayer, and T.W. Sigmon, J. Appl. Phys. **48** (1977) 4234.
  15. Z.T. Kuźnicki, J. Thibault and F. Chautain-Mathys, Journ. du Club Surfaces et Interfaces, Grenoble, 1-2 February.1996; E-MRS Spring Meeting, Strasbourg, France, 3-7 June 1996, and E-MRS First Polish-Ukrainian Symposium "New Photovoltaic Materials for Solar Cells", Cracow-Przegorzaly, Poland, 21-22 October 1996, in press.
  16. A. Lietoila, A. Wakita, T.W. Sigmon, and J.F. Gibbons, J. Appl. Phys. **53** (1982) 4399.