ISSN 1330–0008
CODEN FIZAE4

INTRINSIC POINT DEFECTS IN POLYCRYSTALLINE SILICON

BRANKO PIVAC[a], VESNA BORJANOVIĆ[b] and IVANA KOVAČEVIĆ[a]

[a] *R. Bošković Institute, P. O. Box 180, HR-10002 Zagreb, Croatia*

[b] *Faculty of Electrical Engineering and Computing, Unska 3, HR-10000 Zagreb, Croatia*

Dedicated to Professor Boran Leontić on the occasion of his 70th birthday

Received 29 February 2000; revised manuscript received 5 May 2000
Accepted 10 May 2000

The behaviour of intrinsic point defects in silicon is still an unresolved problem. As they interact with other impurities and influence their diffusion, intrinsic point defects affect electronic properties of the material. Of particular importance is the intrinsic point defect behaviour in polycrystalline silicon due to the presence of very high concentration of structural defects, such as dislocations and grain boundaries of various kinds. A direct observation of point defects is very difficult and therefore it is shown that monitoring of carbon concentration is a very good measure of point defects behaviour. Polycrystalline material supersaturated with carbon represents a particular case when self-interstitials and vacancy generation is significantly retarded up to the highest temperatures, leading therefore to the preservation of carbon supersaturation upon thermal treatments.

PACS numbers: 78.50.Ge UDC 537.312, 537.311.322

Keywords: polycrystalline silicon, intrinsic point defects, interaction with other impurities, electronic properties, supersaturation with carbon

1. Introduction

Intrinsic point defects in silicon, such as self-interstitials and vacancies together with light and non-doping impurities (carbon and oxygen), have been already shown by Foell et al. [1] to be important in the development of microdefects in silicon single crystal and to influence crystal electronic properties. On the other hand, polycrystalline silicon grown by various methods for use in low-cost solar-cell manufacture presents a challenging situation to analyse in terms of effect of point defects on material structure and properties. A variety of extended structural defects such as dislocations, coherent and noncoherent twin boundaries and grain boundaries are inhomogenously distributed in the material, and concentration of impurities like carbon and oxygen is often very high. The impact of extended defects on the electronic properties has been recognized and extensively studied, however, influence of point defects on electronic properties is still unknown. Polycrystalline silicon material often exhibits different responses of electronic properties during processing from those of single crystals. This may be due to a wider range of possible interactions among extended defects, intrinsic point defects and present impurities.

In this paper, we study one such polycrystalline material, silicon sheet produced in a form of a closed-shape hollow polygon by edge-defined film-fed growth (EFG) technique. This material is highly supersaturated with substitutional carbon, in concentrations ranging from 5 to above 10×10^{17} atoms/cm^3. While carbon concentration in the bulk material is very high, the as-grown EFG silicon has interstitial oxygen concentration generally below the room-temperature detection limit, near 1×10^{16} atoms/cm^3, when grown in an inert gas ambient. However, oxygen concentration can be increased to about 10^{17} atoms/cm^3 by the addition of oxygen-containing gases to the growth ambient [3]. Moreover, additional non-interstitial oxygen is found to be present in this material, since interstitial oxygen concentration is increased upon prolonged high-temperature annealing [4]. Nevertheless, even at maximum concentration of oxygen found in EFG materials, carbon still exceeds the interstitial oxygen level.

The point defects in the as-grown crystal is commonly deduced from the study of etch pits and Cu decoration [2]. Their distribution reflect the pattern of underlying microdefects which cannot usually be imagined in transmission electron microscopy (TEM). Such study was performed on EFG polycrystalline material [5], and the shallow etch pits were observed and their existence attributed to copper decoration of swirl defects during Syton polishing. However, it was not consistently reproduced in Cu decoration experiments. It was also shown that impurities increase electrical activity of dislocations and grain boundaries, although there were no indications of microdefects acting as a nucleation site for impurities in the EFG polysilicon. Moreover, TEM studies of EFG silicon sheet defect structure [6] have not revealed any microscopic defects that could be associated with the saucer pits down to resolution level of about 10 nm.

There have been suggestions that intrinsic point defects and microdefects influence electronic properties of EFG polysilicon [3], and recently new results on gold [6] and platinum [7] diffusion indicate that the EFG lattice contains sinks for silicon self-interstitials (Si_I) not present in single-crystal silicon.

The purpose of this paper is to show that intrinsic point defect population in EFG polycrystalline silicon is entirelly different from the corresponding one in single-crystal silicon.

2. *Experiment*

Experiments were performed on carbon-doped Czochralski-grown (CZ) single-crystal silicon samples with carbon and oxygen concentrations of 2.5×10^{17} and 3.5×10^{17} atoms/cm^3, respectively, and on as-grown EFG ribbons with carbon concentration of about 8×10^{17} atoms/cm^3 and oxygen below the detection limit of IR technique (about 10^{16} atoms/cm^3) in oxygen-lean samples grown in inert atmosphere and about 10^{17} atoms/cm^3 oxygen and about the same carbon content in oxygen-rich samples grown in oxidizing ambients.

IR spectra were taken in the wave-number range from 5000 to 400 cm^{-1} with a Bruker IFS 113v Fourier-transform IR spectrometer at room temperature with a 4 cm^{-1} resolution and with a beam diameter of 1 cm. In order to evaluate oxygen and carbon concentration, a differential technique was used with a floating-zone oxygen and carbon-free sample as a reference. The conversion factor used to calculate the carbon concentration was 1.1×10^{17} atoms/cm^3 (ANSI/ASTM F 121-81) and for oxygen it was 2.45×10^{17} atoms/cm^3 (ANSI/ASTM F 121-80).

All samples were cleaned by removing about 30 μm from both surfaces with the CP-4 etch. Aluminum and gold were evaporated through the shadow masks on the clean surface to form ohmic (gold) and Schottky barrier (aluminum) contacts, respectively. Both $I-V$ and $C-V$ measurements were taken to insure the integrity of the diode characteristics. The DLTS spectra were taken with a SULA Technologies spectrometer. Sample temperature was ramped from 80 to 350 K, and spectra were taken at window rates from 0.2 to 50 ms.

Point defects were introduced homogeneously through the bulk of material by irradiation with γ-rays from a ^{60}Co source to the dose of 300 Mrad at room temperature.

3. Results and discussion

3.1. Self-interstitials in polycrystalline silicon

To study silicon self-interstitials in polycrystalline material, we analysed substitutional carbon behaviour in such material, and from the interaction of the intrinsic point defects and present impurities the information on intrinsic point defects behaviour was derived.

Substitutional carbon concentration in the various silicon samples after different steps of isochronal thermal annealing is presented in Fig. 1. As shown in the figure, carbon-doped single-crystal CZ sample exhibits a strong reduction in substitutional carbon concentration after annealing in the temperature range 600 – 800 °C. Similar results for the monocrystalline oxygen- and carbon-doped silicon were already reported in the literature [8,9]. In particular, it was shown by Shimura [8] that annealing at 750 °C for only 6 h reduces carbon concentration in CZ samples from 5×10^{17} atoms/cm^3 to below the detection limit. Even if carbon was present in a rather low concentration (4×10^{16} atoms/cm^3), annealing at temperatures up to 850 °C led to a very rapid removal of carbon from the substitutional positions, so that its presence is no longer detectable by IR spectroscopy [10]. When such CZ samples are annealed above 850 °C, carbon concentration recovers almost completely. However, we have shown that after recovery at 950 °C, further annealing at higher temperatures (up to 1150 °C) causes again a significant and irreversible decrease of carbon concentration (triangles in Fig. 1).

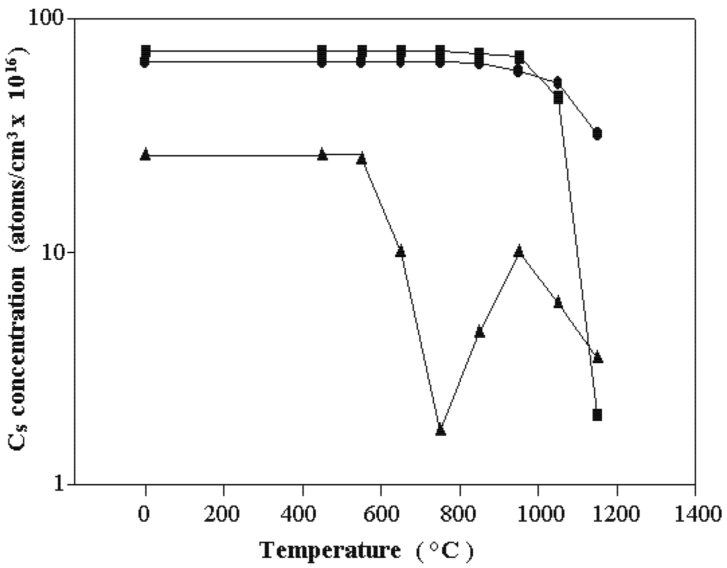

Fig. 1. Carbon concentration in single crystalline CZ sample (triangles), EFG samples grown in inert atmosphere (dots) and EFG samples grown in oxydizing atmosphere (squares).

In polycrystalline EFG silicon, both oxygen-rich and oxygen-lean (squares and dots in Fig. 1), substitutional carbon concentration does not seem to be affected by a long thermal annealing up to about 1000 °C. This occurs despite the fact that carbon concentration in these samples was much higher than the solubility limit for all given temperatures [11]. We analysed various samples grown in different conditions, in inert and oxidizing ambient, and found that they all follow very closely the curves described by dots and squares, respectively, shown in Fig. 1 [12].

Contrary to the behaviour of single-crystal CZ samples, the substitutional carbon concentration in polycrystalline material seems not to be affected by long thermal treatments up to about 1000 °C, irrespectively of the oxygen presence in the bulk of EFG samples. A decrease is observed only upon annealing at highest temperature (1150 °C, as shown in Fig. 1), and in this particular case, oxygen presence plays a significant role. It is shown in Fig. 1 that in polycrystalline material, oxygen presence enhanced substitutional carbon reduction at highest temperatures of annealing for more than one order of magnitude. Although many candidates (incoherent twin boundaries, dislocations, grain boundaries, etc.) as possible nucleation centres for carbon precipitation are already present in as-grown EFG material, prolonged annealing (72 h) in the 650 – 850 °C temeprature range did not affect carbon concentration as in single crystals.

In single-crystalline CZ samples, carbon removal from the substitutional sites upon annealing at 750 °C is explained by C-O interactions and complex defect formation [13]. Contrary to that, no such effect was observed in polycrystalline material, irrespectively of oxygen presence in the bulk. Therefore, oxygen presence in the polycrystalline EFG material seems to play a different role than in single crystals.

Figure 2 compares a differential spectrum of the oxygen-rich polycrystalline sample heated at 1050 °C for 72 h to the same sample heated at 950 °C for the same period of time in the previous step. This figure nicely illustrates the effect of 1050 °C annealing step, when a significant portion of substitutional carbon is removed, as indicated by a large negative peak at 605 cm^{-1}. At the same time, a broad compound peak ranging from 800 to 1000 cm^{-1}, with two pronounced maxima placed at 819 and 883 cm^{-1}, was formed as found earlier in similar samples [4,14,15]. Disappearance of the substitutional carbon confirms that the newly formed broad band is carbon related.

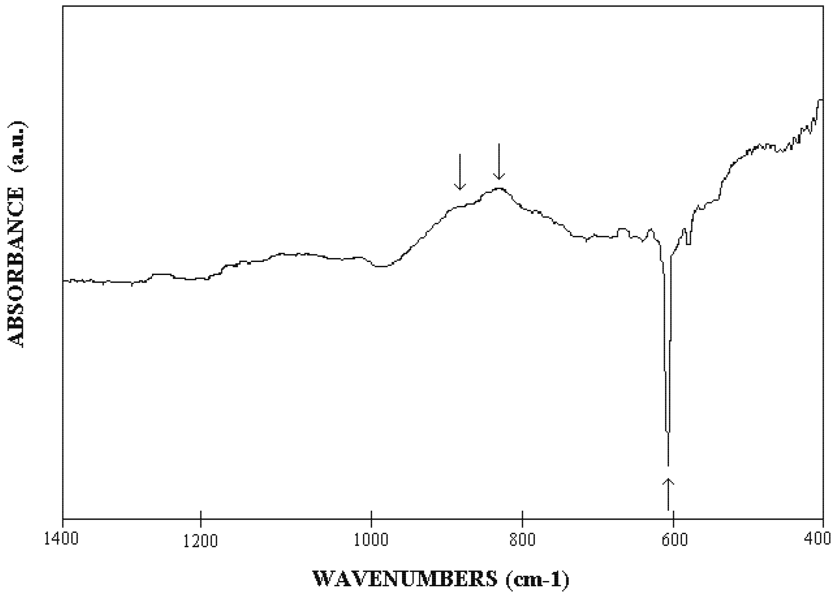

Fig. 2. Differential IR spectrum of EFG oxygen-lean sample annealed at 1050 °C *, compared to the same sample annealed at 950* °C *for 72 h. Arrows indicate maxima at 819 and 883* cm^{-1}.

A similar result was found by Bean and Newman [11] in CZ single-crystal silicon, and it was attributed to carbon precipitation in the form of SiC particles. On the other hand, Shimura [8] attributed the appearance of a broad peak around 850 cm^{-1}, after annealing the CZ crystals in the temperature interval from 750 to 1000 °C, to the formation of the perturbed C (3) centre consisting of an interstitial carbon atom surrounded by several interstitial oxygen atoms [16].

The presented results are explained with the following model. Carbon is very stable in its substitutional position in the silicon lattice, and can be moved only with great difficulty and with the help of silicon self-interstitials (Si_I) due to the unfavourable volume change and strain arising from its smaller effective atomic radius compared to silicon. Self-interstitials are also found to enhance carbon diffusion [17]. Comparing to the CZ single-crystal silicon, EFG polycrystalline silicon is found to be a completely different enviroment for the carbon, as this polycrystalline material is an extremely poor in silicon self-interstitials. This has also been shown by the gold diffusion studies [18] which suggest that present lattice defects have an effective absorption coefficient for self-interstitials which is about a factor of ten greater than in CZ silicon. These defects consist of grown-in and creep-induced dislocations, and microdefects manifesting in shallow etch pits. Moreover, the EFG growth process involves extremely rapid cooling with interface temperature gradients of the order of 1000 °C/cm, which inhibits further microdefect growth and precipitation. These conditions, along with the high carbon supersaturation, lead to a Si_I-poor lattice.

On the other hand, oxygen is known for playing an important role in enhancing Si_I concentration in CZ silicon during the annealing, due to the known effect of Si_I emission during oxygen precipitation [19]. Therefore, for oxygen-poor EFG, the initial shortage of Si_I might be the cause of the different carbon behaviour in comparison to the CZ material. On the other hand, even for oxygen-rich type of EFG material, in spite of significant portion of oxygen present in the bulk, overall carbon behaviour is the same, and the significant difference appears only at the highest temperatures of annealing. This means that for such type of material, even with the substantial oxygen present in the bulk, thermal treatments that usually produce oxygen precipitation (and, therefore, Si_I generation) are inefficient. The lack of Si_I impact on carbon content is due to the fact that sinks for Si_I are more effective than the generation centres. Moreover, as we did not observe oxygen precipitate peaks in IR spectra taken at intermediate temperatures, oxygen precipitation process seems to be retarded in EFG materials.

The arguments also favour the assignment of the perturbed C(3) configuration to part of the broad IR spectrum between 800 and 1000 cm^{-1}, developed in EFG silicon after high temperature annealing (as shown in Fig. 2). The same arguments exclude the possibility of SiC formation in the EFG material. Energetically favoured SiC formation in the silicon lattice requires Si_I presence. On the other hand, sufficient Si_I concentration is available only with the simultaneous precipitation of oxygen in a carbon supersaturated lattice. In oxygen-lean EFG materials, this is obviously not possible. However, as demonstrated, even in the case of oxygen-rich EFG material, this was not the case.

3.2. Vacancies in polycrystalline silicon

Carbon diffusion in silicon was first studied by Newman et al. [20] and later with comparable results by Rollert et al. [21], so that the diffusion properties of this impurity are well known. Carbon is mainly dissolved as substitutional carbon with substitutional solubility which is known [20,21]. It was considered that carbon diffuses via kick-out mechanism

$$\mathrm{C}_s + \mathrm{Si}_i \leftrightarrow \mathrm{C}_i$$

where C_i denotes highly-mobile carbon interstitial. As a result of this kick-out reaction, the $\mathrm{Si_I}$'s are consumed and, consequently, $\mathrm{Si_I}$'s undersaturation in carbon supersaturation regions may reach values of 0.01 in comparison with its equilibrium concentration [22]. Recently however, Scholz et al. [23] have shown that accurate description of carbon diffusion profiles are only possible if the Frank-Turnbull mechanism, involving vacancies, is additionally taken into account.

$$\mathrm{C}_i + \mathrm{V} \leftrightarrow \mathrm{C}_s$$

The above equation describes the Frank-Turnbull mechanism where the carbon interstitials C_i interact with vacancies. Unlike earlier models for correct carbon diffusion which suggested additional hidden source of self-interstitials [24], considering Frank-Turnbull model implies considering supersaturation of vacancies in carbon-rich region.

There have been some suggestions [7] that polycrystalline EFG material is heavily depleated with self-interstitials and supersaturated with vacancies. Moreover, combining results from platinum diffusion, where platinum recombines with single vacancy, and positron annihilation studies which are sensitive to the total number of vacancies, it is suggested that in EFG polycrystalline material the total concentration of vacancies would range from 10^9 cm^{-3} to 10^{13} cm^{-3}.

To check the vacancy generation and redistribution, we irradiated the polycrystalline EFG material with γ-rays from a ^{60}Co source. Fig. 3 shows the results of DLTS spectroscopy on such irradiated and nontreated samples. The dominant level observed in the spectrum is H(0.38), the same as observed in as-received samples [25] and related to larger structural defects. On the other hand, several new centres, H(0.13), H(0.17), H(0.27) and H(0.36), are created in the irradiated sample. The observed centres, according to the literature, are attributed to H(0.17) divacancy [26] and H(0.27) to divacancy-oxygen (V2O) centre [27]. H(0.36) is, however, attributed to two energetically closely-spaced levels, one of which is $\mathrm{C}_i\mathrm{O}_i$ complex and another $\mathrm{C}_s\mathrm{C}_i$ complex [28]. We have thus shown that the γ-ray irradiation of EFG polycrystalline silicon produces vacancies and vacancy-related defects which are otherwise nonmeasurable in as-received material. Since the detection limit of DLTS technique is about 10^{11} defects/cm^3, our finding is in accordance with earlier suggestions [7].

Nevertheless, our experiments have shown that generation of vacancies and vacancy-related defects in carbon doped EFG polycrystalline material is significantly retarded in comparison with carbon-free single crystals [28].

Summarizing, we have shown that even in spite of carbon supersaturation in EFG polycrystalline material, vacancy generation is significantly suppressed, very much like the suppression of self-interstititals generation in the same material.

Therefore, even considering vacancies as a driving vehicle for carbon diffusion, suppression in vacancy generation means reduced carbon diffusion as discussed earlier.

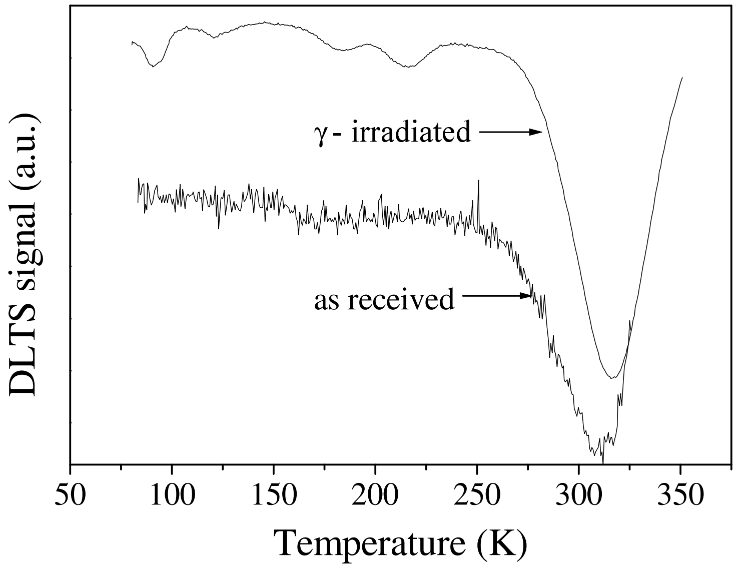

Fig. 3. DLTS spectra of as-received and γ-irradiated EFG polycrystalline silicon.

4. *Conclusion*

We have shown that supersaturated carbon concentration in EFG polycrystalline silicon is a very good measure of intrinsic point-defect population in such materials. It is shown that substitutional carbon diffusion is retarded up to the highest temperatures. Considering that carbon diffusion in silicon, according to the present theories, may use both self-interstitials or vacancies, their generation is significantly reduced in the intermediate temperature range in polycrystalline material.

References

[1] H. Foell, U. Gösele, and B. O. Kolbesen, J. Crystal Growth **52** (1977) 907.

[2] P. J. Roksnoer, J. Crystal Growth, **68** (1984) 596.

[3] J. P. Kalejs, in *Silicon Processing for Photovoltaics II*, eds. C. P. Khattak and K. V. Ravi, North-Holland, Amsterdam (1987), p. 187.

[4] B. Pivac and U. V. Desnica, J. Appl. Phys. **65** (1989) 4759.

[5] S. A. McHugo and W. D. Sawyer, Appl. Phys. Lett. **62** (1993) 2519.

[6] W.-S. Yang, W. J. Taylor, B. P. R. Marioton and U. Gösele, in *Polycrystalline Semiconductors II*, eds. J. H. Werner and H. P. Strunk, Springer, Berlin (1991) p. 236.

[7] J. P. Kalejs, J. of Crystal Growth **128** (1993) 298.

[8] F. Shimura, J. Appl. Phys. **59** (1986) 3251.

[9] F. Shimura, T. Higushi, and R. S. Hockett, Appl. Phys. Lett. **53** (1988) 69.

[10] F. M. Livingston, S. Messoloras, R. C. Newman, B. C. Pike, R. J. Stewart, M. J. Binns, W. P. Brown and J. G. Wilkes, J. Phys. C **17** (1984) 6253.

[11] A. R. Bean and R. C. Newman, J. Phys. Chem. Solids **32** (1971) 1211.

[12] B. Pivac, M. Amiotti, A. Borghesi, A. Sassella, and J. Kalejs, J. Appl. Phys. **71** 3785 (1992) 3785.

[13] F. Shimura, J. P. Baiardo, and P. Fraundorf, Appl. Phys. Lett. **46** (1985) 941.

[14] B. Pivac, in *Polycrystalline Semiconductors*, vol. 35, Springer Proceedings in Physics, eds. J. Werner, H. J. Müller, and H. P. Strunk, Springer, Berlin (1989) p. 170.

[15] B. Pivac, J. Phys. D **23** (1990) 83.

[16] F. Shimura, Y. Ohnishi, and H. Tsuya, Appl. Phys. Lett. **38** (1982) 867.

[17] J. P. Kalejs, L. A. Ladd, and U. Gösele, Appl. Phys. Lett. **45** (1984) 268.

[18] W.-S. Yang, W. J. Taylor, B. P. R. Marioton, and U. Gösele, in *Proc. POLYSE Conf.*, eds. J. Werner and H. Strunk, Springer, Berlin (1991) p. 236.

[19] C. Claeys and J. Vanhellemont, in *Proc. 2nd GADEST*, ed. H. Richter (Acad. Sciences G.D.R., 1987) p. 3.

[20] R. C. Newman and J. Wakefield, J. Phys. Chem. Solids **19** (1961) 230.

[21] F. Rollert, N. A. Stolwijk, and H. Mehrer, Mater. Sci. Forum **38-41** (1989) 753.

[22] R. Scholz, U. Gösele, J.-Y. Huh and T.Y. Tan, Appl. Phys. Lett. **72** (1998) 200.

[23] R. F. Scholz, P. Werner, U. Gösele, and T. Y. Tan, Appl. Phys. Lett. **74** (1999) 392.

[24] H. Rücker, B. Heinemann, W. Röpke, R. Kurps, D. Krüger, G. Lippert, and H. J. Osten, Appl. Phys. Lett. **73** (1998) 1682.

[25] V. Borjanović, I. Kovačevic, B. Šantic, and B. Pivac, Mater. Sci. & Eng. B, in press.

[26] M. Asghar, M. Zafar Iqbal and N. Zafar, J. Appl. Phys. **73** (1993) 4240.

[27] M.-A. Trauwaert, J. Vanhellemont, H. E. Maes, A.-M. Van Bavel and G. Langouche, Appl. Phys. Lett. **66** (1995) 3057.

[28] G. Ferenci, C. A. Londos, T. Pavelka, M. Somogyi and A. Mertens, J. Appl. Phys. **63** (1988) 183.

[29] M. H. Yuan, D. C. Peng, Q. Z. Peng, Y. H. Zhang, J. Q. Li and G. G. Qin, J. Appl. Phys. **71** (1992) 1182.

INTRINSIČNI TOČKASTI DEFEKTI U POLIKRISTALINIČNOM SILICIJU

Svojstva intrinsičnih točkastih defekata još su uvijek neriješen problem. Svojim međudjelovanjem s drugim defektima i utjecajem na njihovu difuziju, oni mijenjaju elektronska svojstva materijala. Posebno su važni intrinsični točkasti defekti u polikristaliničnom siliciju zbog prisutnosti velikih koncentracija strukturnih defekata, kao što su dislokacije i granice kristalića raznih vrsta. Izravno je opažanje točkastih defekata vrlo teško, pa je stoga promatranje koncentracije ugljika vrlo dobar način određivanja svojstava točkastih defekata. Polikristalinični silicij prezasićen ugljikom predstavlja poseban slučaj u kojemu je snažno usporeno stvaranje vlastitih intersticijskih defekata i praznina sve do najviših temperatura, što stoga vodi na čuvanje ugljikovog prezasićenja u toplinskim obradama.