

# Depth Analysis of Crystalline Silicon Used for Radiation-Hard Detectors

S.J. MOLOI<sup>a,\*</sup> AND M. MCPHERSON<sup>b</sup>

<sup>a</sup>Department of Physics, University of South Africa, P.O. Box 392, Pretoria 0003, South Africa

<sup>b</sup>Centre for Postgraduate Studies, Cape Peninsula University of Technology, P.O. Box 652, Cape Town 8000, South Africa

(Received 17 March, 2017; in final form 8 August, 2017)

Depth analysis of metal-doped crystalline silicon by the X-ray photoelectron spectroscopy technique is presented in this work. The results from this technique are used to complement those from previous techniques. The metals diffused into the silicon are gold, platinum, erbium, and niobium. In silicon, these metals induce defects that are responsible for relaxation behaviour of the material. Relaxation material is radiation-hard since the effects of radiation on devices fabricated on the material are suppressed. Considerable amounts of gold, platinum, and niobium are found in the silicon bulk. The results of this work are in good agreement with those reported earlier on the same samples using the Rutherford backscattering technique. The spectra of the natural contaminants, carbon and oxygen, are also analysed in this work.

DOI: [10.12693/APhysPolA.132.1387](https://doi.org/10.12693/APhysPolA.132.1387)

PACS/topics: silicon, diffusion, XPS, detectors

## 1. Introduction

Crystalline silicon needs to be modified in the bulk in order to improve the properties of devices fabricated on the material. The properties have to be improved since devices fabricated on the material fail to operate efficiently as radiation detectors. The failure to operate efficiently is due to damage that occurs in the material by incident high energetic particles [1, 2]. As they become incident onto the material, the particles penetrate the material and collide with the semiconductor lattice. The incident particles transfer sufficient energy to the silicon to displace an atom within the lattice out of its normal position such that interstitial atoms and vacancies are generated in the bulk of the material [3]. The result is that the lattice structure of the material changes and this degrades the performance of the devices.

In order to improve the properties of the devices, the silicon material can be doped with metals such as gold, platinum, erbium, or niobium [4–11]. These metals are responsible for a change in material behaviour from lifetime to relaxation [9–11]. In relaxation material,  $\tau_D \gg \tau_0$  while in lifetime material,  $\tau_D \ll \tau_0$  [12–15]. Here,  $\tau_D$  is the dielectric relaxation time and  $\tau_0$  is the minority carrier recombination lifetime [12–15]. In relaxation material the effects of radiation are suppressed [5, 9] such that the damage is minimal. In this case the Fermi level of the material is not affected by any incident radiation [16]. This is because the Fermi level in relaxation material becomes pinned at midgap [17].

Depending on their nature and their amount in silicon, the metals can generate defects that have characteristics

similar to those generated by radiation [11]. Thus, the metals can render the material useless to fabricate devices that can be used as radiation detectors. It is, therefore, very important that the concentration of metal required to cause relaxation behaviour in the material is known. It is also essential that diffusion mechanisms of these metals into silicon are investigated so that their undesired effects are minimized while the desired effects are improved.

In studying the diffusion mechanisms of gold and platinum into silicon, it has been found that the diffused atoms occupy both substitutional and interstitial sites [4, 6]. The interchange of atoms between the sites during diffusion is controlled by the dissociative and the kick-out mechanisms [4, 6]. In the former process the diffusion involves silicon vacancies, while in the latter one the diffusion involves self-interstitials. The diffusion mechanisms of erbium and niobium into silicon need to be studied as well, since they exhibit similar effects as those of gold and platinum.

In this work, depth analysis by X-ray photoelectron spectroscopy (XPS) was carried out on metal-coated *p*-type silicon prior to, and after, metal diffusion. The spectrum peaks generated from the metal-coated samples are found to be reduced and shifted towards higher sputter depth regions which indicates that the metals are found in the silicon bulk after the diffusion process. The spectra peaks of the gold, platinum, and niobium-coated samples are found to be higher than those of silicon after the diffusion process. This indicates that the concentration of the metals is higher than that of silicon at the depth of 20 nm and 10 nm in case of niobium. These results are in agreement with those obtained earlier from the Rutherford backscattering spectroscopy (RBS) technique [18]. However, in the work reported before based on RBS results, the diffusion was evaluated by noting a change in spectra after the annealing process. These metals, dif-

\*corresponding author; e-mail: [moloisj@unisa.ac.za](mailto:moloisj@unisa.ac.za)

fused in the bulk, convert silicon from a lifetime to a relaxation material [11].

## 2. Experimental technique

XPS measurements were carried out on the metal-coated *p*-type silicon samples prior to, and after, the diffusion process. The measurements were done using the Physical Electronics Quantum (PEQ) 2000 instrument at the Council for Scientific and Industrial Research (CSIR) in South Africa. The samples were annealed at 900 °C for 18 h to allow diffusion of the metals into the silicon bulk. An Al  $K_{\alpha}$  X-ray source with energy of 1486.6 eV was used to excite electrons from the surface of the sample to an entrance slit of hemisphere analyser. The diameter of the X-ray beam was 100  $\mu\text{m}$ . The mean analysing energy of the analyser was 58.7 eV. This meant that only electrons of this kinetic energy will be detected. The detection angle was set at 45° from a surface that is normal to the sample. For depth profiling measurements, the sample surfaces were sputtered with 2.0 keV argon ions while the binding energy regions of the specific element were being monitored. The measurements were performed from the top surface to the bulk of the sample and were carried out at room temperature and at vacuum pressures below  $10^{-9}$  mbar. A detailed description of the samples and their preparations has been outlined elsewhere [19].

## 3. Results and discussion

The XPS spectra of silicon, gold, platinum, erbium and niobium are presented here. Carbon and oxygen are the main contaminants of the samples and their spectra are also presented but not thoroughly discussed as they are not for our concern. The spectra are presented in the following sections with the relative atomic concentration as a function of the sputter depth.

### 3.1. Gold-deposited samples

Figure 1 shows the XPS spectra for gold-deposited samples (a) prior to and (b) after the diffusion process. In Fig. 1a the spectra show that carbon with 22% atomic concentration and oxygen with 75% atomic concentration dominate on the surface of the silicon (depth of 0 nm). A sudden decrease in concentration is observed for both elements and they disappear completely at a depth of 4 nm. Since the two elements are found only at the surface, they do not have an effect in the bulk and this is why they are not for our concern for this sample.

Gold is not observed on the surface (at a depth of 0 nm). This means that a layer of carbon and oxygen covered the gold surface after deposition. Gold with atomic concentration of 100% is observed at a depth of 5 nm. The concentration of gold decreases until it becomes zero at 18 nm. The atomic concentration of silicon increases sharply to 98% and becomes almost constant up to a depth of 30 nm. An increase in silicon concentration corresponds to a decrease in gold concentration. This shows that there is no interface layer formed between gold and silicon [19]. It is evident from these results that at depths greater than 18 nm only silicon atoms dominate.

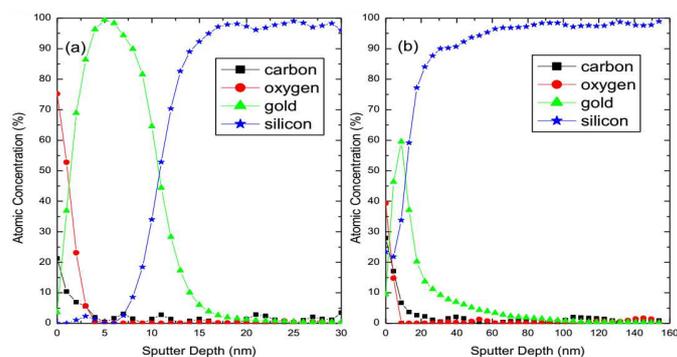


Fig. 1. XPS depth profile for gold-deposited samples prior to (a) and after (b) the diffusion process.

In Fig. 1b the spectra show carbon with 40% atomic concentration and oxygen with 28% atomic concentration on the surface. The amount of these contaminants decreases significantly with depth and disappears at 10 nm and 23 nm, respectively. These results show that carbon and oxygen do not diffuse into the bulk. Gold is also found on the surface with a 10% atomic concentration and this shows that not all the gold deposited is diffused into the silicon. Gold is seen deep into the bulk at depths of over 80 nm.

Silicon is also observed with 26% atomic concentration on the surface of the samples after the diffusion process. The concentration decreases slightly before a depth of 7 nm and then increases sharply to 90% at 25 nm. After a depth of 26 nm the spectrum shows a tendency to almost saturate. This sharp decrease of gold concentration that corresponds to a sharp increase of silicon concentration indicates that there is no interface layer formed between gold and silicon after the diffusion process. The presence of silicon on the surface of the sample shows that silicon was exposed when gold was diffusing into the bulk. There is indication of a good mix of gold and silicon up to depths of 80 nm.

The gold peak has been reduced from 100% to 60% and shifted from 5 nm to 18 nm after diffusion. The reduction of the peak indicates that the concentration of gold has been reduced on the surface while the shift of the peak to a higher sputter depth indicates that gold has diffused into the bulk of the silicon.

### 3.2. Platinum-deposited samples

Figure 2 shows the XPS spectra for the platinum-deposited samples (a) prior to and (b) after the diffusion process. The spectra presented in Fig. 2a show that carbon with 55% atomic concentration and oxygen with 14% atomic concentration dominates on the surface of the silicon. A decrease in the concentration of carbon to 47% is observed after a depth of 1 nm and then it almost remains constant up to a depth of 8.5 nm. At a depth of 9 nm the concentration decreases and becomes 0% after the sputter depth of 15 nm. Since the concentration is not decreasing sharply at a depth lower than 10 nm

as observed in Fig. 1a for gold-deposited samples, these results show that there is a thick layer of carbon on the surface of the silicon.

The oxygen spectrum, on the other hand, disappears completely after a depth of 2 nm to show that oxygen is very thin on the surface of the silicon. The 22% atomic concentration of platinum is also found on the surface of the silicon indicating that platinum is not completely covered by carbon and oxygen layers. Platinum concentration increases sharply to 55% at a depth of 1.5 nm and then becomes almost constant up to a depth of 8.5 nm. After a depth of 9 nm the platinum spectrum follows the one of carbon and showing a sharp decrease in concentration to 4% at 16 nm. Carbon and platinum might be bonded to each other since their spectra reach the saturation and show a sharp decrease in concentration at the same depth.

These results explain the small peak that was observed in the RBS results for the platinum-deposited sample [18]. This sample was contaminated by carbon during sample preparation since the peak was also observed [18] in the RBS result that were obtained immediately after the deposition. The spectrum in Fig. 2a shows silicon with 9% atomic concentration on the surface which decreases rapidly until it becomes 0% at a depth of 6 nm. After 7.5 nm the silicon concentration increases sharply to 92% at 17.5 nm and then becomes constant up to 30 nm. The sharp increase of silicon concentration corresponds to the sharp decrease of carbon and platinum concentrations to show that there is no interface layer formed between platinum and silicon. Even though they are bonded, carbon and platinum are not found in the silicon bulk. This is shown in Fig. 2a where silicon atoms dominate after 18 nm.

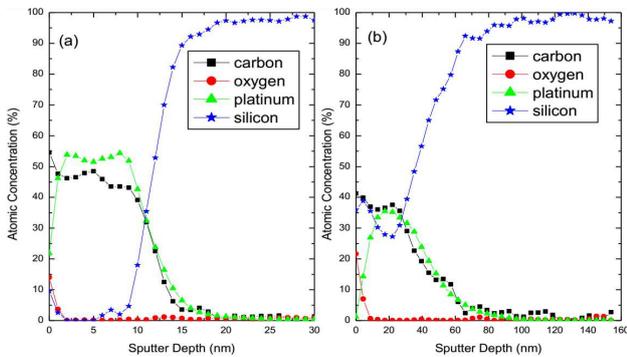


Fig. 2. XPS depth profile for platinum-deposited samples prior to (a) and after the (b) diffusion process.

In Fig. 2b spectra show carbon with 41% atomic concentration on the surface and it remains almost constant up to a depth of 30 nm. After a depth of 31 nm, the carbon concentration decreases with depth. Comparing Fig. 2a and 2b, it can be noted that in Fig. 2b the carbon concentration has decreased at low depth. This is an indication that carbon concentration has decreased on the surface and diffused into the silicon. As it was observed in

RBS results [18], the shifting of small peak towards the lower energy indicates that carbon atoms diffused into the silicon. The oxygen spectrum, on the other hand, shows 22% atomic concentration on the surface. Since the layer is very thin on the surface, the concentration decreases and becomes 0% at low depth.

Platinum is found on the surface with 2% atomic concentration. The concentration increases to 35% at 20 nm. After 21 nm the concentration decreases rapidly to 0% at 70 nm. Silicon is also observed with 35% atomic concentration on the surface. The silicon concentration decreases slightly as the depth increases to 30 nm and then increases sharply to 92% at 40 nm. After 41 nm the concentration remains almost constant at 98% up to 160 nm. As it was explained earlier, a sharp decrease of carbon and platinum concentrations that corresponds to a sharp increase of silicon indicates that there is no interface layer formed between platinum and silicon. A presence of silicon on the surface shows that it was exposed when platinum was diffusing into the bulk.

The platinum peak has been reduced from 55% to 35% and shifted to 20 nm after diffusion. This reduction of the peak indicates that the platinum concentration of platinum has been reduced on the surface while the shifting to higher sputter depth shows that platinum has diffused into the bulk of the silicon.

### 3.3. Erbium-deposited samples

Figure 3 shows the XPS spectra for erbium-deposited samples (a) prior to and (a) after the diffusion process. In Fig. 3a the spectra show that carbon with 47% atomic concentration and oxygen with 40% atomic concentration dominate on the surface of the silicon. The carbon concentration decreases sharply to 6% at the sputter depth lower than 2 nm to show that it is very thin on the surface. After 2.5 nm, the spectrum shows an oscillation between 0 and 5% carbon concentration until it disappears completely at 20 nm. This oscillation could be due to fluctuation in the XPS system. Unlike in the case of gold-deposited and platinum-deposited samples, the oxygen concentration in this case decreases to 25% and then remains almost constant up to the sputter depth of 12.5 nm. After 13 nm the concentration decreases to 5% at 15.5 nm and then to 0%. This behaviour suggests that there is a thick layer of oxygen on the surface. Even though the XPS results show the high relative concentration of oxygen on the surface, it has to be noted that the sample was contaminated after the deposition since the oxygen peak was not observed in the RBS measurements [18]. These results show that erbium reacts vigorously with oxygen.

The erbium concentration increases sharply from 11% on the surface to 65% at the sputter depth less than 2 nm. After the depth of 2.5 nm the spectrum shows an oscillation between 74 and 65% erbium concentration up to the depth of 12 nm. After 12.5 nm the concentration decreases sharply to 5% at 20 nm and then becomes 0% after 21 nm.

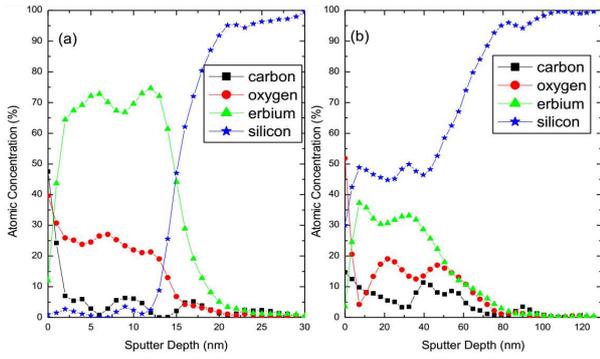


Fig. 3. XPS depth profile for erbium-deposited silicon samples prior to (a) and after (b) the diffusion process.

Figure 3a shows the 0% atomic concentration of silicon on the surface. This indicates that silicon has not been exposed to the surface. At the depth of less than 11.5 nm the spectrum shows an oscillation of silicon concentration between 0 and 3%. This oscillation as it was said before could be due to fluctuation in the XPS system. At the depth higher than 12 nm the sharp increase of silicon concentration corresponds to the sharp decrease of erbium concentration to show that there is no interface layer formed between erbium and silicon.

In Fig. 3b the spectra show carbon with 15% atomic concentration and oxygen with 53% atomic concentration on the surface. The carbon concentration decreases steadily to 3% at 25 nm. After 30 nm the concentration increases to 11% at 40 nm and then decreases steadily until it becomes 0% at 70 nm. At the depth less than 7 nm the oxygen concentration decreases to 4.5% and then increases to 20% at 20 nm. After 21 nm the spectrum shows an oscillation between 15% and 18% of oxygen concentration up to 48 nm and then decreases to 4% at 78 nm until it becomes 0% at 80 nm. Spectra show that carbon and oxygen concentration becomes zero after the longer sputter depth. This indicates that carbon and oxygen are thick on the surface of the sample.

Erbium is found on the surface with the concentration of 3.5%. The erbium concentration increases to 37% at the depth of less than 7 nm and then decreases to 28% at the depth of 18 nm where it remains almost constant up to 33 nm. After 34 nm the concentration decreases rapidly to 2.5% at the depth of 80 nm and then becomes zero. The silicon spectrum, on the other hand, shows 30% atomic concentration on the surface indicating that silicon was exposed when erbium was diffusing into the bulk. At the depth less than 7 nm the concentration increases to 49% and then oscillates between 50% and 45% up to 40 nm. After 41 nm the concentration increases sharply to 95% and then saturates. The sharp increase of silicon concentration corresponds to the sharp decrease of erbium concentration to show that there is no interface layer formed between them.

The highest peak of erbium has been reduced from 66% to 31% and shifted to a higher sputter depth after

diffusion. This reduction of the peak indicates that erbium has been reduced on the surface while the shifting shows that platinum has diffused into the bulk of silicon. Unlike in the case of gold and platinum, the spectrum of erbium is lower than that of silicon indicating that the concentration of erbium diffused is low in all sputter depths.

### 3.4. Niobium-deposited samples

Figure 4 shows the XPS spectra for niobium-deposited samples (a) prior to and (b) after the diffusion process. In Fig. 4a the spectra show carbon with 71% atomic concentration and oxygen with 25% atomic concentration dominating on the surface. The carbon concentration decreases sharply to 5% at the depth lower than 2.5 nm to show that it is very thin on the surface. After 2.5 nm, the concentration increases to 8% and then it remains almost constant up to 10 nm until it becomes 0% at higher sputter depth. The oxygen concentration increases to 55% at the depth lower than 2.5 nm. At the depth higher than 2.5 nm the concentration decreases to 2% until it becomes 0% at the depth higher than 8 nm. These results show that oxygen and carbon are thick on the surface.

A very low relative atomic concentration of niobium is observed on the surface. The concentration increases to 51% at the depth lower than 7 nm and then decreases to 3% at the depth of 13 nm. After 13 nm the concentration remains constant up to 30 nm. It can be noted in Fig. 4a that there is a very low atomic concentration of silicon on the surface. After 2.5 nm the silicon concentration increases to 5.5% and then remains constant up to 6 nm. At the depth higher than 6 nm the concentration increases sharply to 86% at 13 nm and then increases gently to 93% at 17.5 nm. The rapid increase of silicon concentration corresponds to the sharp decrease of niobium concentration to show that there is no interface layer formed between them. After 17.5 nm the silicon concentration remains almost constant at 95% up to 30 nm. A decrease in carbon concentration is not rapid after 7.5 nm indicating that is found in the bulk.

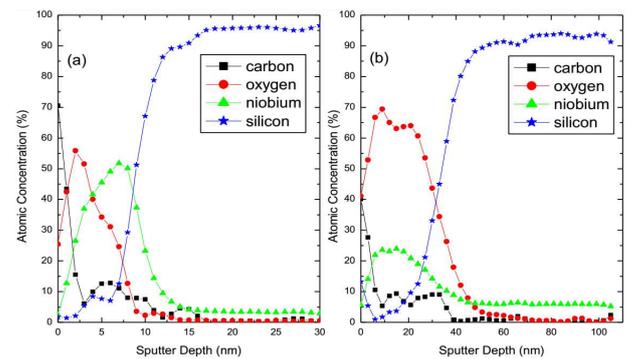


Fig. 4. XPS depth profile for niobium-deposited samples prior to (a) and after (b) the diffusion process.

In Fig. 4b the spectra show carbon with 40% atomic concentration and oxygen with 41% atomic concentration on the surface. The carbon concentration decreases

rapidly to 5% at 9 nm and oscillates between 5 and 10% up to 32 nm. After 32 nm the concentration becomes 0%. At a depth of less than 10 nm the oxygen concentration increases sharply to 70% and then decreases to 64% at 22.5 nm. After 23 nm the concentration decreases sharply to 3% at 50 nm and then becomes 0%. The concentration of oxygen has increased from 53 to 70% and shifted from 7 nm to 18 nm after diffusion process. This may suggest that niobium reacts vigorously with oxygen.

Niobium is found on the surface with the relative concentration of 5%. The niobium concentration increases to 24% at the depth less than 10 nm and then remains almost constant up to 18 nm. After 19 nm the concentration decreases gently to 8% at 40 nm and then it remains constant. The silicon spectrum, on the other hand, shows 14% atomic concentration on the surface to show that it was exposed when niobium was diffusing into the bulk. At the depth less than 6 nm the silicon concentration decreases sharply to 0% and then increases gently up to 15% at 18 nm. After 20 nm the concentration increases sharply to 92% at 50 nm and then remains constant. The sharp increase of silicon spectrum corresponds to the sharp decrease of oxygen and niobium spectra to show that there is no interface layer formed between niobium and silicon.

It can be noted that niobium peak has been reduced from 51% to 25% and shifted to a higher sputter depth of 10 nm after diffusion process. This reduction of the peak indicates that niobium has reduced on the surface while the shift to higher sputters depth shows that it has diffused into the bulk.

#### 4. Overall discussions

XPS measurements were carried out on metal-deposited samples prior to and after the diffusion process. This work adds on that presented on RBS results presented earlier [10, 18] since the diffusion of metals was speculated. The results presented here are thus used to explain features that could not be explained by the RBS data and also confirm that metals diffuse in silicon at 900 °C for 18 h of annealing. The highest peaks of gold, platinum and niobium are found to be higher than that of silicon indicating that the metals are found with considerable atomic concentration at the sputter depth of 20 nm in silicon. The results indicate that gold, platinum and niobium diffuse with more considerable amount into silicon at an annealing temperature of 900 °C if the process is done over 18 h. At this annealing temperature and over this time the diffusion profile of gold and platinum in silicon is U-shaped and is dominated by the kick-out [20–22]. It has to be noted that the diffusion mechanisms of niobium are currently not known.

The erbium spectrum, on the other hand, is lower than that of silicon in the whole sputter depth. This indicates that the amount of diffused erbium is low. This is due to a very low diffusion coefficient that the metal has in silicon at 900 °C [23]. The diffusion profile of erbium in silicon is currently not well understood. It has been reported that

at the annealing temperature of 900 °C for 30 min, erbium likely diffuses interstitially in silicon [24]. Contrary, it was also reported that most of erbium atoms in silicon occupy substitutional sites [25]. These contradictory studies indicate that there is no definite answer about the diffusion mechanisms of erbium in silicon.

#### 5. Conclusion

The results from the XPS measurements show that there is no interfacial layer formed between silicon and the deposited metal layer. The results also show that the spectrum peak of metal-doped samples gets reduced and shifted towards higher depths after the diffusion process. This reduction of the peak heights indicates that the amount of metals on the silicon surface has been reduced. The shift of the peak indicates a presence of metal in the silicon bulk. Both results show that the metal from the surface of the silicon has diffused into the bulk. These diffused metals have been shown to render the silicon material relaxation-like. The XPS technique can thus be used to complement the RBS technique in depth profiling of our defect-engineered silicon.

#### Acknowledgments

We thank M. Msimanga at Tshwane University of Technology for assistance with preparation of the samples and the CSIR for availing their PEQ 2000 instrument to us.

#### References

- [1] M. Martini, T.A. McMath, *Nucl. Instrum. Methods* **79**, 259 (1970).
- [2] V.A.J. Van Lint, *Nucl. Instrum. Method Phys. Res. A* **253**, 453 (1987).
- [3] M. Moll, H. Feick, F. Fretwurst, G. Lindstrom, C. Schutze, *Nucl. Instrum. Methods Phys. Res. A* **388**, 335 (1997).
- [4] U. Gosele, W. Frank, A. Seeger, *Appl. Phys.* **23**, 361 (1980).
- [5] R.L. Dixon, K.E. Ekstrand, *Radiat. Protect. Dosim.* **17**, 527 (1986).
- [6] Y.K. Kwon, T. Ishikawa, H. Kuwano, *J. Appl. Phys.* **61**, 1055 (1987).
- [7] J.L. Benton, J. Michel, L.C. Kimerling, D.C. Jacobson, Y.H. Xie, D.J. Eaglesham, E.A. Fitzgerald, J.M. Poate, *J. Appl. Phys.* **70**, 2667 (1991).
- [8] H. Pettersson, Grimmeiss, L. Tilly, Schalz, H. Kerkow, *Semicond. Sci. Technol.* **8**, 1247 (1993).
- [9] M. McPherson, T. Sloan, B.K. Jones, *J. Phys. D Appl. Phys.* **30**, 3028 (1997).
- [10] M. Msimanga, M. McPherson, *Mater. Sci. Eng. B* **127**, 47 (2006).
- [11] S.J. Moloi, M. McPherson, *Physica B* **404**, 2251 (2009).
- [12] W. van Roosbroeck, *Phys. Rev.* **123**, 474 (1961).
- [13] H.J. Queisser, *IOP Conf. Series* **15**, 145 (1972).
- [14] M. Ilegems, H.J. Queisser, *Phys. Rev. B* **12**, 1443 (1975).

- [15] N.M. Haegel, *Appl. Phys. A* **53**, 1 (1991).
- [16] V.N. Brudnyi, S.N. Grinyaev, V.E. Stepanov, *Physica B* **212**, 429 (1995).
- [17] M. McPherson, *Physica B* **344**, 52 (2002).
- [18] S.J. Moloi, M. McPherson, *Vacuum* **104**, 51 (2014).
- [19] J.W. Pankow, *Surface Analysis of Stressed and Control Tin Oxide Thin Films on Soda Lime Glass*, presented at the National Centre for Photovoltaics and Solar Program Review Meeting, Denver (USA), 2003.
- [20] F. Morehead, N.A. Stolwijk, W. Meyberg, U. Gosele, *Appl. Phys. Lett.* **42**, 690 (1983).
- [21] S. Coffa, L. Calcagno, S.U. Campisano, G. Calleri, G. Ferla, *J. Appl. Phys.* **64**, 6291 (1988).
- [22] O. Boström, B. Pichaud, M. Regula, J.C. Bajar, G. Blondiaux, O.A. Soltanovich, E.B. Yakimov, A. Lhorte, J.B. Quoirin, *Mater. Sci. Eng. B* **71**, 166 (2000).
- [23] J.H. Shin, G.N. van den Hoven, A. Polman, *Appl. Phys. Lett.* **67**, 377 (1995).
- [24] M. Needels, M. Schlüter, M. Lannoo, *Phys. Rev. B* **47**, 15533 (1993).
- [25] Y.S. Tang, Zhang Jingping, K.C. Heasman, B.J. Sealy, *Solid State Commun.* **72**, 991 (1989).