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Characterization of poly-Si thin films deposited by magnetron sputtering onto Ni prelayers

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A method of producing a polycrystalline silicon thin film on a foreign substrate without subsequent annealing has been developed. Thermally evaporated 5–100 nm thick Ni films served as prelayers for magnetron sputtered Si thin films. A continuous film was obtained as a result of metal induced growth of polysilicon during low temperature (below 600 °C) deposition. The film uniformity is promising for large area device applications. The influence of the Ni prelayer thickness on the grain size of thus obtained films was investigated. Atomic force microscopy and cross-sectional scanning electron microscopy studies revealed features in the 150–600 nm size range while x-ray diffraction and Raman spectra analysis predicted 50–100 nm diam randomly oriented grains and a complete absence of an amorphous phase. The carrier lifetime was evaluated to be 11 μs. © *2000 American Institute of Physics.* [S0021-8979(00)03907-4]

I. INTRODUCTION

How to reduce the thermal budget for Si crystallization and, hence, the technological cost is still a question of great concern today. A number of attractive techniques have been proposed during the past several years in order to limit the process temperature below the glass softening point. The recrystallization of predeposited amorphous Si thin films at low temperatures is the most widespread approach and usually results in a uniform crystalline structure possessing large grains. On the other hand, this method suffers from drawbacks such as the high cost of the laser annealing or the long time required for furnace crystallization. In our previous work,[1] we reported the properties of the poly-Si thin film grown by a liquid phase growth (LPG) technique at a temperature of around 600 °C. This approach first employed in our laboratory in 1993[2] utilized a 50–500 nm layer of Sn or In/Ti deposited onto polished Mo substrates coated with SiO$_2$. This was followed by the Si deposition during which a metal–Si melt was formed and remained on the surface leaving behind a poly-Si film. As a result, Si films revealed 1–20 μm crystal size but a serious uniformity problem existed. By this time, the effect of a metal presence on the Si crystallization parameters was reported by several research groups. Liu and Fonash[3] introduced a thin Pd film deposited on a predeposited *a*-Si film which reduced crystallization temperature from 700 to 500 °C. Hayzelden and Batstone[4] studied the enhancement of Ni-implanted Si film crystallization by formation of NiSi$_2$ precipitates which served as nucleation sites for Si crystals. Further work on Ni implantation[5] made possible the thin film transistor fabrication with a mobility of 120 cm^2/V s at temperatures below 500 °C. The metal induced crystallization (MIC) technique was also applied to annealing of direct current (dc) magnetron sputtered[6]

Si films doped with Ni by cosputtering. Recently, in the In/Ti process, we attempted to replace Ti with Pd, Al, and Ni. In the case of a Ni prelayer, the uniformity of the Si film was considerably improved but was still unsatisfactory, which led us from LPG to metal induced growth (MIG) of poly-Si thin films. In the following sections we describe the MIG approach and present selected structural properties of the resulting Si film. In addition, we discuss a possible mechanism of MIG.

II. EXPERIMENT

In this study, a 300 nm thick SiO$_2$ film was grown on a single crystal silicon wafer by plasma enhanced chemical vapor deposition. This substrate was chosen for convenience and will later be replaced by a thin metal, glass, or plastic. Ni was thermally evaporated on the SiO$_2$/Si substrate at a base pressure in the lower 10^{-6} Torr range. The thickness of the Ni film was monitored with an approximate error of 5% and was varied from 5 to 100 nm in order to investigate the influence of Ni thickness on deposited Si film properties. The substrates were cleaned by sequential ultrasonic processing for 2 min in acetone, methanol, and de-ionized water before and after Ni evaporation and immediately loaded into the dc magnetron sputtering system to avoid excessive Ni oxidation in the air. The silicon thin film deposition started at a base pressure of 2–3×10^{-7} Torr. The deposition was performed in a 5% H$_2$/Ar atmosphere where Ar and H$_2$ were, respectively, used as a carrier gas and to saturate dangling bonds at grain boundaries. All runs were carried out at a fixed pressure of 1 mTorr inside of the chamber and a power of about 50 W. Two *n*-type Si targets with different resistivity values of 0.02 and 0.006 Ω cm were utilized for this study to examine the effect of source doping on the Si films properties. The substrate–target distance was kept at 8 cm for all runs.

First, the samples were heated in the presence of 5% H$_2$/Ar mixture for 30–40 min. Then, the target was

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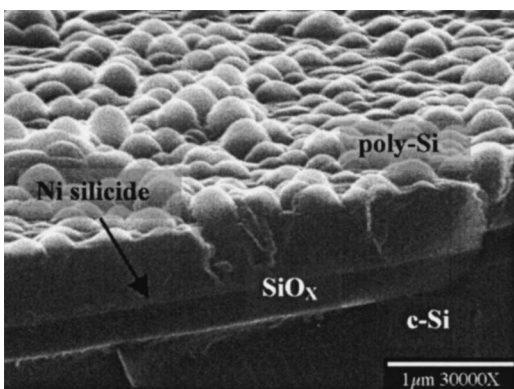
FIG. 1. Cross-sectional SEM photo of 0.6 μm poly-Si thin film deposited onto 15 nm Ni prelayer at 525 °C.

plasma cleaned at a low power of 3 W for 8–10 min. Sputtering began after temperature completely stabilized and normally took place for 1 h at a deposition rate of 0.6 μm/h. The final polysilicon film thickness of 600±50 nm was roughly kept constant across all runs in order to reduce the number of variables in the beginning of this study. Finally, the samples were cooled to room temperature in the same H_2/Ar ambient. The surface morphology was investigated by means of atomic force microscopy (AFM) and scanning electron microscopy (SEM). X-ray diffraction (XRD) and Raman spectroscopy measurements were used for the grain size and crystallinity characterization. X-ray photoelectron spectroscopy (XPS) depth profiling was performed to determine Si and Ni concentrations throughout the film thickness.

III. RESULTS

In Fig. 1, a cross-sectional SEM photo reveals 0.5–0.6 μm features on the surface of the Si film deposited onto a 15 nm thick Ni layer at 525 °C. However, the maximum crystal size calculated from the FWHM of the corresponding peaks of the XRD spectra appears to be 100 nm. Thus, from XRD data, these features on the film surface were assumed to be clusters of grains with smaller size. We have studied a number of samples by means of AFM and XRD and found an obvious correlation between the grain size given by XRD and maximum cluster size on the film surface.

Varying the thickness of the Ni prelayer produced a clear correlation between Ni thickness and the grain size. Figure 2 shows AFM pictures of surface morphology taken for two samples with different Ni thickness prepared during the same deposition run at 550 °C by sputtering a 0.006 Ω cm target. It is seen that the maximum cluster size of approximately 250–300 nm corresponds to the Si film deposited on the 5 nm thick Ni prelayer, while the 50 nm thick Ni film provides clusters in 400–450 nm size range. Cluster size dependence on the Ni prelayer thickness for the samples prepared at different deposition temperatures is shown in Fig. 3. The cluster size and, respectively, grain size increase with Ni thickness up to the corresponding thickness of 20–30 nm and then drop again, indicating the presence of some maximum. It was noticed that with increase in the target resistivity this maximum tends to be shifted to the lower values of the Ni
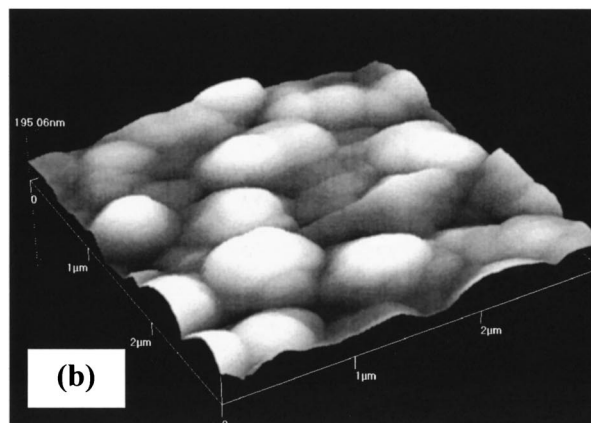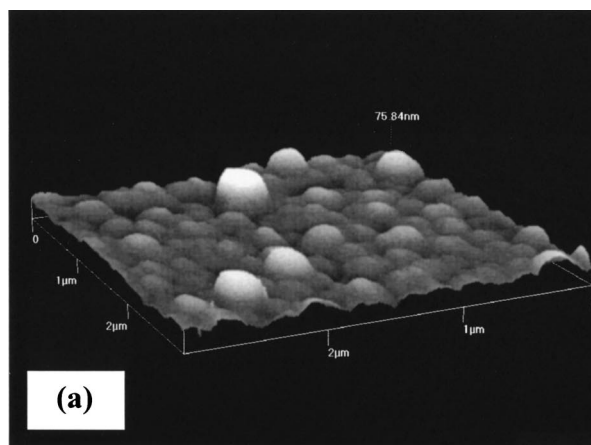

FIG. 2. AFM pictures of surface morphology for the samples deposited at 550 °C on Ni prelayer with thickness: (a) 5 nm and (b) 50 nm.

thickness. Thus, a series of samples prepared by sputtering of the 0.02 Ω cm target showed an improved cluster size for the 15–25 nm thick Ni film.

The XRD analysis of all samples also indicates a strong dependence between Ni thickness and grain size. The latter was calculated from the FWHM of corresponding crystalline peaks at $d = 3.14$ Å (111), $d = 1.92$ Å (220), and $d = 1.64$ Å (311) using the Scherrer equation. Moreover, the XRD data
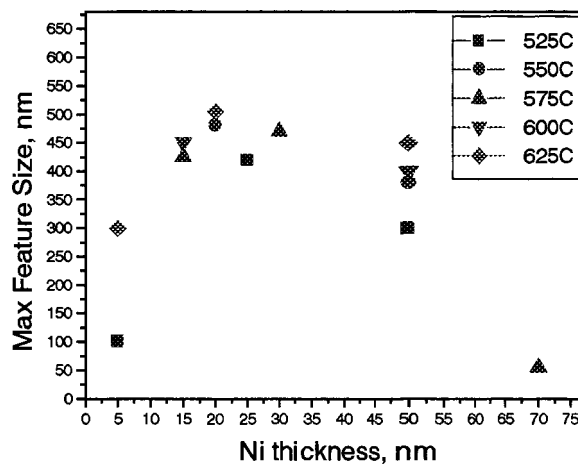

FIG. 3. The influence of the Ni prelayer thickness on maximum cluster size for different deposition temperatures investigated by AFM.
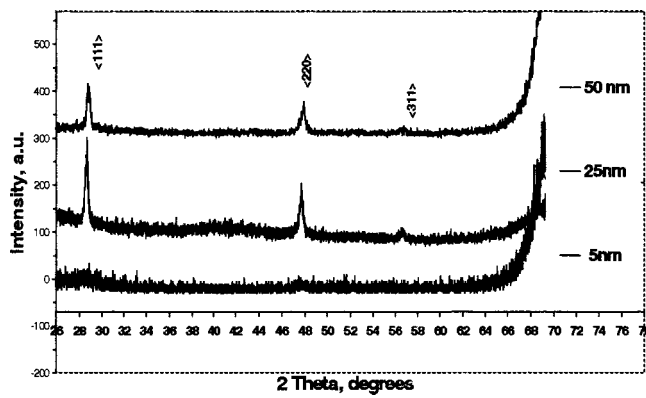
FIG. 4. XRD spectra of poly-Si thin films deposited at 525 °C with various Ni prelayer thicknesses of 5, 25, and 50 nm.

FIG. 6. Raman spectra of Si thin films deposited at 550 °C by sputtering from an 0.02 Ω cm target on the Ni prelayer with thicknesses of 15 and 23 nm, respectively.

confirm the existence of the aforementioned maximum in the grain size, which also occurs at the Ni thickness values in the 20–40 nm range. Figure 4 shows the XRD spectra taken for poly-Si thin films deposited onto, respectively, 5, 25, and 50 nm thick Ni prelayers at the deposition temperature of 525 °C. The peak narrowing is clearly seen for the Ni thickness of 25 nm in comparison to 50 nm, while the 5 nm thick Ni prelayer gave somewhat noticeable broad peaks at (111) and (220) planes. The intensity and therefore the crystalline portion was found to increase for the sample with 25 nm thickness of Ni as well. It is known that absolute values of the peak intensities cannot be compared for different planes because of the thickness effect of the variation in the angle of incidence and are normally correlated with each other as (111):(220):(311)=100:60:35. The dependence of thus corrected intensity upon the Ni film thickness for a set of samples deposited at 575 °C is shown in Fig. 5. It was noticed in the previous work[4,7] that Ni silicide-mediated crystallization of Si occurred mainly parallel to the ⟨111⟩ direction. Jin et al.[8] reported that Ni induced crystallization of Si resulted in large (110) oriented grains. These observations may not be necessarily applicable for our case since the for-

mation of nuclei and the crystal growth take place simultaneously during deposition. Due to the absence of the (110) reflection, the amount of the (110) texture in our samples could be estimated from the (220) peak. However, we were not able to distinguish whether the (111) or (220) orientation was preferred for the samples at a Ni thickness below 30 nm. Instead, we found a noticeable increase in the (220) orientation at a Ni thickness above 30 nm. The determination of the amount of (100) oriented crystals was not attempted because of the fairly strong (400) peak contributed by the (100) reflection of the single crystal Si wafer.

The high crystallinity of metal induced grown Si films was confirmed by Raman spectroscopy. Two samples with a Ni thickness of 15 and 25 nm deposited at 550 °C by sputtering of the 0.02 Ω cm target were analyzed. The Raman spectra of both samples (Fig. 6) displayed strong peaks in the vicinity of the usual occurrence of the crystalline Si features. An observed peak shift from 515 cm^{-1} (25 nm of Ni) to 516.5 cm^{-1} (15 nm of Ni) was in good agreement with the AFM data for the 0.02 Ω cm target case, which showed that maximum crystal size occurred at the Ni film thickness of 15 nm. The value of FWHM did not exceed 15 cm^{-1} for both peaks. The deconvolution of Raman spectra implied the existence of a low intensity feature at 500 cm^{-1} which was attributed to a microcrystalline component and was more intense for the sample with the 25 nm thick Ni underlayer. No peaks were observed in the vicinity of 480 cm^{-1}, which indicated no evidence of the presence of an amorphous phase. The XRD analysis performed on a series of samples deposited directly (without a Ni prelayer) on SiO_2/Si substrates at the temperatures in the 525–625 °C range did not reveal any crystalline peaks on the spectra. Also, Raman spectra did not contain any peaks above 490 cm^{-1}. It allowed us to assume that in contrast to the metal-induced grown polysilicon, the Si film without a Ni prelayer remains amorphous up to at least 625 °C. In addition, the carrier lifetime measurement carried out on the surface of our Si film grown on a Ni underlayer resulted in 11 μs, which corresponds to satisfactory electrical properties.
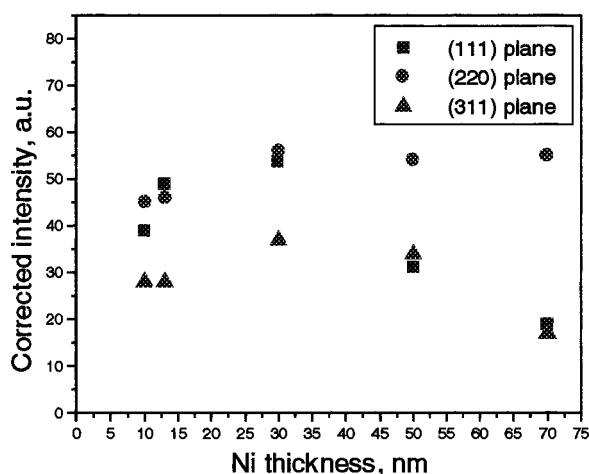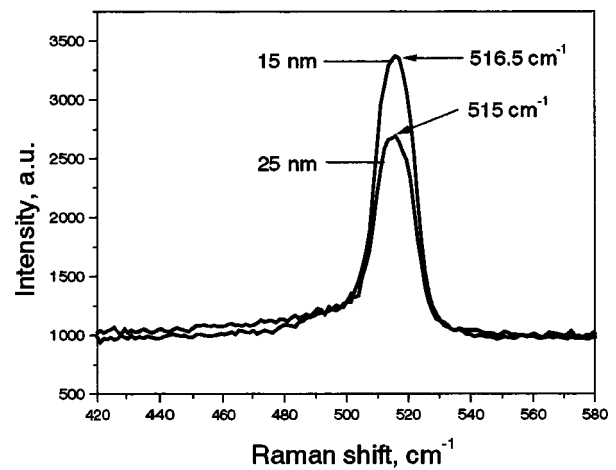

FIG. 5. The effect of Ni prelayer thickness on the crystal orientation of the Si thin films deposited at 575 °C. The intensities are corrected using the ratio (111):(220):(311)=100:60:35.

IV. DISCUSSION

The most striking observation in this study was, perhaps, an obvious structural dependence of the Si film on the thickness of a Ni underlayer. Lee *et al.*[5] studied annealing of P-implanted *a*-Si films in the presence of an ultrathin nickel layer introduced on top of the films and stated that the thickness of a Ni layer had almost no effect on film characteristics when it was varied from 2 to 50 Å. In that work, the microstructure was characterized only in terms of crystallinity and no values of the grain size were given. We propose the following mechanism in our observations. The thickness of the Ni prelayer represents a particular source of Ni atoms available for the Ni silicide formation and, as a consequence, a thicker Ni film gives rise to a thicker Ni silicide. As one could notice in the experimental part, the Si film processing involves breaking the vacuum between Ni and Si deposition steps. Naturally, a very thin film of NiO_x inevitably forms on the surface of the Ni layer. At low Ni concentrations, even a small number of impurities, such as oxygen atoms, are able to hinder the process of the nucleation of the silicide crystals. Up to a certain thickness of the Ni layer (25 nm in the case of a 0.006 Ω cm target), the defect-assisted nucleation becomes less competitive with an increase in Ni thickness, which leads to an improved Si grain size. When Ni concentrations become even higher, they start to play a major role in the final silicon grain size determination (it is known that higher concentration of nucleation sites usually corresponds to a larger number of grains with smaller size) and grain size decreases with Ni thickness. Summarizing the above discussion, the observed maximum in the Si grain size may be attributed to the competition of two mechanisms: defect-controlled and Ni diffusion-controlled nucleation phenomena.

Since the MIG technique provided a poly-Si film with improved structural properties, it is tempting to investigate the mechanism responsible for the silicon growth in detail. We could not find any instances of previous work on metal induced growth of polycrystalline silicon thin films. Instead, we review here some earlier work on the metal induced crystallization of predeposited *a*-Si. Jin *et al.*[8] studied the annealing of *a*-Si films covered with a 5–10 nm thick Ni layer and concluded that Ni induced crystallization occurred via: (1) silicide formation at the Ni–Si interface with (2) subsequent breakup of the silicide layer due to further growth of Si grains, and (3) transport of silicide nodules through the *a*-Si film. Furthermore, it was concluded[4] that the silicide-mediated crystallization of *a*-Si implied the formation of epitaxial Si crystals on the faces of the octahedral $NiSi_2$ precipitates. The driving force for $NiSi_2$ precipitates was assumed[9] to be the difference in free energy associated with the transformation of metastable *a*-Si to stable *c*-Si. Another explanation[10] is based on the Ni atomic diffusion into *a*-Si since Ni is known to be a fast interstitial diffuser in Si. Ni silicide formation then takes place in the entire film volume through the recrystalization process. The XPS depth profile [Fig. 7(a)] collected for the 0.05 μm poly-Si film on a 15 nm thick Ni prelayer indicated a decrease in Ni concentration closer to the Si surface. An 0.6 μm Si/25 nm Ni sample

(a)
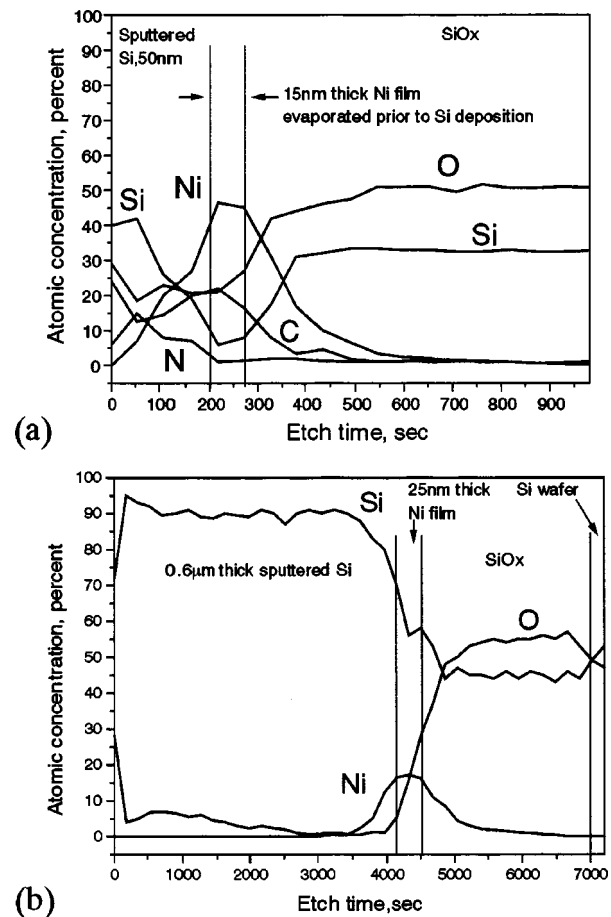

(b)

FIG. 7. XPS depth profiles for samples deposited at 575 °C: (a) 0.05 μm Si/15 nm Ni; (b) 0.6 μm Si/25 nm Ni.

showed no Ni presence throughout the Si film volume except in the 40–50 nm region confined to the Ni–Si interface, as shown in Fig. 7(b).

The precise composition of the nickel silicide is also questionable. Tu and Mayer[11] reported that the formation of nickel silicide between a film of Ni and a *c*-Si wafer exhibits a sequential growth of three phases. The first phase, nickel-rich Ni_2Si, forms at the interface between Ni and Si at temperatures as low as 200 °C assisted by a diffusion-controlled phenomenon and grows until the Ni is consumed. The next phase, NiSi, starts to form at the Ni_2Si–Si interface at temperatures around 350–400 °C. Nickel monosilicide is thermally stable up to 750 °C when the transition from NiSi to $NiSi_2$ is initiated by a nucleation-controlled phenomenon. Recently, XPS analysis[12] distinguished $NiSi_2$ from NiSi, which differed by less than 1 eV in binding energy and showed that the silicide phase transition between NiSi and $NiSi_2$ occurred above 900 °C. In the case of amorphous silicon, the above formation temperatures were found to be noticeably lower than that for *c*-Si, which can be attributed to additional free energy released through the silicon crystallization.[11,13] Lien *et al.*[13] reported the existence of the Ni disilicide at 400 °C. Yoon *et al.*[9] observed the formation of $NiSi_2$ precipitates at a temperature less than 350 °C. Surprisingly, the first and only phase to form as a result of the annealing of Ni-implanted *a*-Si thin films was $NiSi_2$ as re-

ported by Cammarata *et al.*[14] *In situ* transmission electron microscopy carried out by Hayzelden and Batstone[4] also revealed the formation of $NiSi_2$ precipitates immediately upon heating while, as we mentioned before, $NiSi_2$ was the last phase to form in a thin Ni film case. According to the above observations, the deposition temperature in the range from 525 to 600 °C was high enough for the Ni disilicide formation. Moreover, we believe that in MIG, $NiSi_2$ can theoretically form at even lower temperatures than that for the MIC case. During silicon film deposition, Si atoms arriving at the substrate can freely move on the surface in order to minimize the growing film–substrate interfacial energy and, respectively, a barrier for nucleation. Meantime, breaking and remaking of silicon covalent bonds is necessary for the recrystallization of amorphous silicon. From XPS depth profiling, the existence of $NiSi_2$ precipitates throughout the whole film volume might not be a necessary prerequisite for MIG and the continued Si crystal growth occurs due to the impingement of Si atoms onto a poly-Si surface.

V. CONCLUSIONS

In summary, we propose a new technological method of depositing a uniform, good quality poly-Si film by dc magnetron sputtering using the MIG technique. This method avoids an expensive and time consuming postdeposition treatment of the Si film because the crystal formation occurs during deposition. The poly-Si film was shown to consist of crystals with up to 0.1 μm diameter without an indication of an amorphous phase. The existence of an optimum Ni prelayer thickness, which provides the Si film with maximum grain size, was found. The carrier lifetime of 11 μs indicated good electrical properties.

[1] W. A. Anderson, B. Jagannathan, and E. Klementieva–Guliants, Prog. Photovoltaics **5**, 433 (1997).
[2] R. L. Wallace and W. A. Anderson, Mater. Res. Soc. Symp. Proc. **358**, 883 (1995)
[3] G. Liu and S. J. Fonash, Appl. Phys. Lett. **55**, 660 (1989).
[4] C. Hayzelden and J. L. Batstone, J. Appl. Phys. **73**, 8279 (1993).
[5] S.-W. Lee, T.-H. Ihn, and S.-K. Joo, Appl. Phys. Lett. **69**, 380 (1996).
[6] O. Schoenfeld, T. Hempel, X. Zhao, and Y. Aoyagi, Thin Solid Films **261**, 236 (1995).
[7] S. Y. Yoon, K. H. Kim, C. O. Kim, J. Y. Oh, and J. Jang, J. Appl. Phys. **82**, 5865 (1997).
[8] Z. Jin, G. A. Bhat, M. Yeung, H. S. Kwok, and M. Wong, J. Appl. Phys. **84**, 194 (1998).
[9] S. Y. Yoon, J. Y. Oh, C. O. Kim, and J. Jang, J. Appl. Phys. **84**, 6463 (1998).
[10] H. Kim, J. G. Couillard, and D. G. Ast, Appl. Phys. Lett. **72**, 803 (1998).
[11] K. N. Tu and J. W. Mayer, *Thin Films–Interdiffusion and Reactions*, edited by J. M. Poate, K. N. Tu, and J. W. Mayer (Wiley, New York, 1978), p. 359.
[12] E. Maillard-Schaller, B. I. Boyanov, S. English, and R. J. Nemanich, J. Appl. Phys. **85**, 3614 (1999).
[13] C.-D. Lien, M.-A. Nicolet, and S. S. Lau, Phys. Status Solidi A **81**, 123 (1984).
[14] R. C. Cammarata, C. V. Thompson, and K. N. Tu, Appl. Phys. Lett. **51**, 1108 (1987).