Materials Science Forum
ISSN: 1662-9752, Vol. 1124, pp 97-102
doi:10.4028/p-Qq8Six

Submitted: 2023-09-30
Revised: 2024-06-06
Accepted: 2024-06-11
Online: 2024-08-21

Characterization of Very Thin 3C-SiC Epilayers on Si

Marcin Zielinski[1,a*], Marc Bussel[1,b], Marc Portail[2,c], Adrien Michon[2,d], Yvon Cordier[2,e]

[1]NOVASiC; Savoie Technolac; 73375 Le Bourget du Lac cedex; France

[2]CRHEA, CNRS-UPR10, Université Côte d'Azur, rue Bernard Grégory, 06560 Valbonne, France

[a]mzielinski@novasic.com, [b] mbussel@novasic.com, [c]mpo@crhea.cnrs.fr, [d]am@crhea.cnrs.fr, [e]yc@crhea.cnrs.fr

Keywords: 3C-SiC, thickness, FTIR, X-Ray diffraction

Abstract. We verify experimentally to what extent the intensity of 3C-SiC TO peak in infrared reflectance spectrum can be used to estimate the thickness of extremely thin 3C-SiC epilayers on Si. The influence of several Si substrate characteristics (orientation, doping level, back-side surface preparation) on the peak calibration is discussed.

Introduction

The mechanical properties (ex. high elastic modulus) of silicon carbide make this material an interesting candidate for resonating sensors and other Micro Electro Mechanical Systems (MEMS devices). The 3C-SiC epilayers on Si are of particular interest in that field, mainly for fabrication related reasons – the thickness of the resonating device (membrane, beam) is directly determined by the thickness of epilayer which reduces the complexity of processing steps. For various designs of MEMS resonators, noteworthy resonator characteristics are expected for very thin (<500nm) and extremely thin (<200 nm) SiC epilayers [1, 2].

In order to achieve in a reproducible way a desired characteristic of resonating device, the thickness of the epilayer needs to be perfectly controlled. This may seem to be a trivial point; however, two potential difficulties arise.

First is related to the fact that in typical two-step growth process of 3C-SiC on Si (carbonization to create SiC seed, followed by CVD thickening of SiC), a finite thickness of 3C-SiC is deposited already during the carbonization step, through Reactive CVD (R-CVD) mechanism. Furthermore, the R-CVD mechanism remains active during the early stage of CVD step [3]. In other words, the growth rate and duration of CVD step are not the only parameters that affect the final 3C-SiC thickness. The R-CVD contribution (in the range of tens of nm) can easily be neglected when 3C-SiC film is thicker than 1µm. But we need to consider it in our particular case of extremely thin epitaxy.

Second difficulty is related to the metrology aspects. Typically, the thickness of SiC films is estimated from the spectral periodicity of interference fringes of infrared reflectance spectra in the range 1000-7000 cm^{-1}. But the 3C-SiC films considered here are too thin to create periodic fringes in this range.

A possible solution is to take into account another SiC film signature – the transversal optic (TO) phonon peak. Already in 70's, the TO peak intensity was used as thickness indicator of poly 3C-SiC coatings [4]. Later-on, a complete study of carbonization kinetics was based on TO peak analyses [5]. In both cases the peak was observed in transmittance configuration.

In the present contribution we explore experimentally the evolution of 3C-SiC TO peak observed in reflectance configuration and verify to what extent the integrated intensity of this peak can be used as thickness indicator.

Proposed TO Peak Calibration

Figure 1a shows the 3C-SiC/Si reflectance spectra, calculated for different thicknesses (0-2µm) of 3C-SiC film on semi-infinite Si substrate, in typical 400-7000cm^{-1} range (see [6] for calculation

details). For the thicknesses down to ~1µm several interference fringes allow the estimation of 3C-SiC thickness. At 500nm, the interference pattern is limited to one fringe and for lower thicknesses, down to ~150nm, only one intensity minimum remains visible. Its spectral position depends on 3C-SiC thickness, as illustrated in Figure 1c. This means that the film thickness can be estimated from interference phenomena for the films as thin as 150 nm.

For thinner films, the first minimum moves outside the studied spectral range. The TO related feature remains the only 3C-SiC signature. Figure 2b presents the evolution of corresponding spectral region for 3C-SiC thicknesses ranging over 0-2µm: from reststrahlen band at high thickness to peak-like feature for films below ~300nm. We define as "TO peak area", S_{TO}, the difference between the integrated intensity of 3C-SiC/Si and bare Si spectra in arbitrarily chosen range 675-960 cm^{-1}. The TO peak area so defined is an increasing function of 3C-SiC thickness. It saturates progressively as the TO feature transforms from peak to reststrahlen band. For simplicity, in this paper it will be considered that in the thickness range 0-300 nm, S_{TO} is proportional to the film thickness (however, more precise adjustment, as the one represented in Fig.1d, is also possible).

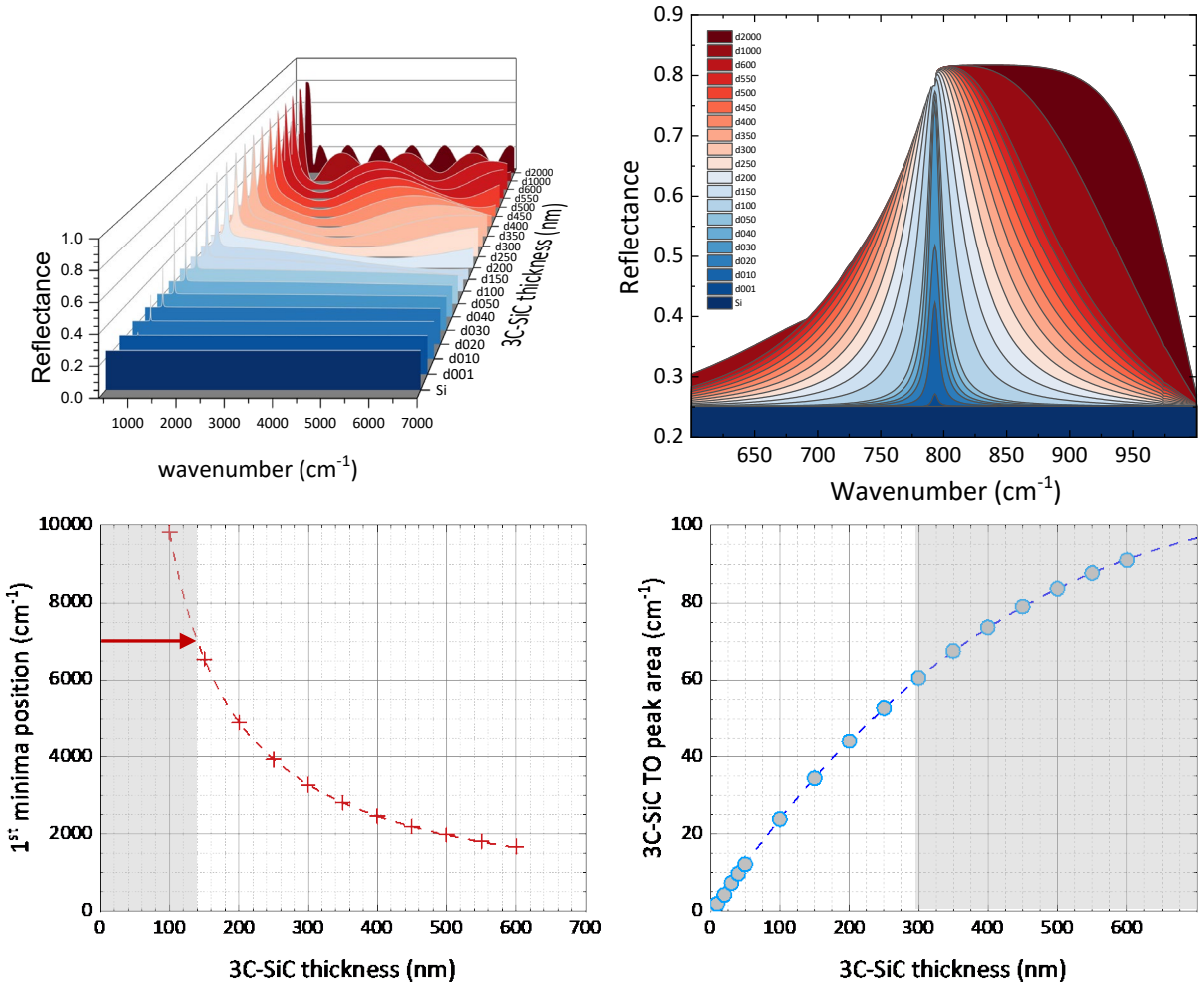

Fig. 1. (a) Simulated spectra of 3C-SiC/Si stack for different thicknesses of 3C-SiC (0-2µm). (b) Zoom on 3C-SiC TO peak region. (c) Evolution of spectral position of reflectance minimum closest to TO peak with 3C-SiC thickness. (d) Evolution of 3C-SiC TO peak area with 3C-SiC film thickness.

Table 1. Characteristics of sample series analyzed in present study

Sample Series	Orientation	Si substrate Resistivity (Ωcm)	Surface	Sample size	CVD info
(A)	(100)	1-10	SSP	14x14 mm²	0-75 min on (A) - (D)
(B)	(100)	>10000	SSP		
(C)	(111)	1-10	SSP		
(D)	(111)	>10000	DSP		
(D_0)	(111)	>10000	DSP	100 mm	0-17 min
(E)	(100)	1-10	DSP	14x14 mm²	with (A) - (D)
(F)	(100)	0.01	SSP		

Experimentally, to establish a scaling factor K between the TO peak area S_{TO} and the film thickness d_{3C}, one can use the films with thicknesses in 150nm – 300nm range, for which the thickness value will be extracted from the position of first interference minimum. After calculating the linear regression $d_{3C} = K \cdot S_{TO}$, the scaling factor K (expressed in nm/cm^{-1} units) will subsequently be used to estimate the thickness of very thin films, for which no interference related information is available.

Experimental Details

CVD setup and sample growth. 3C-SiC thin films were deposited in previously described horizontal, low pressure, resistively heated hot wall CVD system with rotating sample holder [7]. Standard chemistry was used with purified hydrogen (H_2) as carrier gas, high purity (5N) silane (SiH_4) and propane (C_3H_8) as principal precursors. No intentional doping was applied.

Same carbonization step, adapted for both Si(100) and Si(111) substrates, was used in all growth experiments. The conditions of CVD step were also fixed, with very low deposition rate (~0.6µm/h). The only variable parameter was the duration of the CVD step, adjusted between 0 and 75 min.

Two types of growth experiments were performed for the needs of this study: full wafer processes (on 100mm wafers) and multi-sample processes in which several 14x14mm² samples were simultaneously placed in the reactor. Epitaxial growth was performed on Si substrates with various orientations ((100) and (111)), doping levels (lowly doped, ρ>10000 Ωcm; medium doped, ρ=1-10 Ωcm; and, occasionally, highly doped, ρ~0.01 Ωcm) and backside preparation (single side polished (SSP) with rough backside or double side polished (DSP)). The details of samples series are given in Table 1.

Characterizations. Fourier Transform InfraRed (FTIR) reflectance measurements were performed on all the samples in 380-7000 cm^{-1} range with 1 cm^{-1} resolution. X-Ray Diffraction (XRD) measurements (2θ-ω and ω scans of basal plane reflections) were systematically performed on (111) oriented samples from series C and D. The XRD tool was equipped with a Cu X-ray source emitting at the wavelength Kα1 of copper (0.15406 nm) and with a Ge(220) crystal monochromator. The cross-sections of selected samples from series A and C were observed using scanning electron microscopy (SEM).

Experimental Results

Experimental FTIR Spectra. An example of the evolution of 3C-SiC/Si reflectance spectra with CVD step duration across the full measurement range is shown in Figure 2. Spectra were acquired on sample series A (epilayers on Si(100) medium-doped SSP substrates). Previously mentioned spectra features are easy to identify. In particular, interference-related minimum is visible for CVD step duration above 12 min. The TO peak, absent on bare Si wafer even after high temperature annealing, clearly appears after the carbonization step. Its area increases with duration of CVD growth.

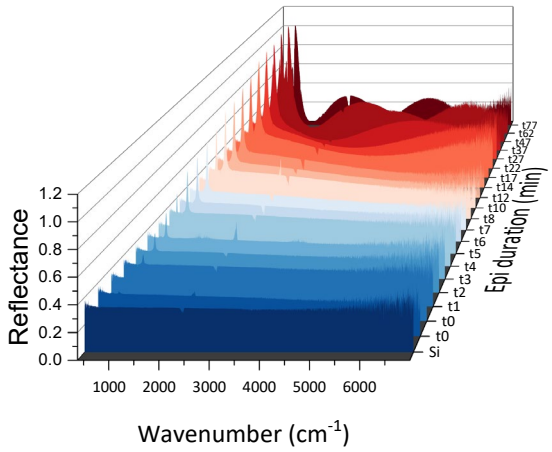

Fig. 2. Evolution of FTIR reflectance spectra with CVD step duration for 3C-SiC films grown on Si(100) SSP substrates.

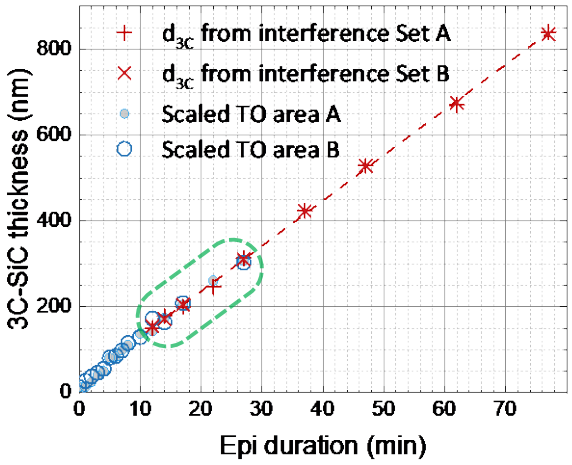

Fig. 3. Overview of thickness measurements on (100) oriented samples (series A and B).

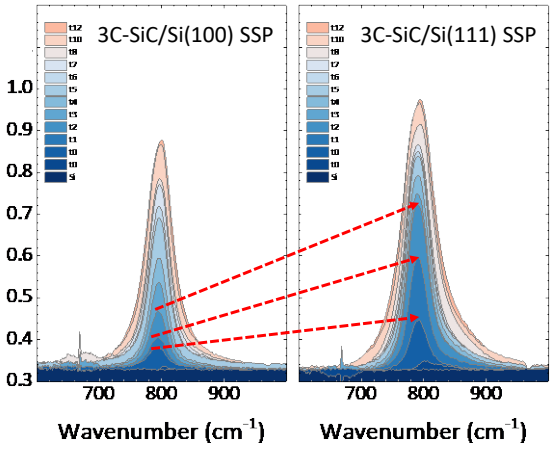

Fig. 4. Comparison of TO spectral region of films grown on (100) and (111) oriented, medium doped, single side polished Si substrate.

Scaling factor. The determination of scaling factor between the TO peak area and the film thickness was based on the samples with CVD step duration of 12-30 minutes. As expected, same value, K=3.85±0.06 nm/cm^{-1} was found for samples from series A and B. In fact, the substrate doping variation between low and medium values does not affect the IR reflectivity spectra. Figure 3 presents an overview of thickness measurements on (100) oriented samples (series A and B) combining the values estimated from TO peak area and from the interference minimum.

3C-SiC(111) versus (100) epilayers. The evolution of IR reflectance spectra in 3C-SiC/Si(111) is qualitatively similar to that reported for (100) orientation. However, directly after carbonization step on Si(111) the intensity of TO peak is higher, and it increases faster in initial phase of CVD step than it was observed on Si(100). This is illustrated in Figure 4.

After ~5 minutes of CVD step, same evolution rate of peak area is observed for (111) and (100) films, suggesting that same scaling factor can be used for both orientations. Faster increase of thickness in the initial stage of CVD step is related to the previously mentioned fact that the R-CVD mechanism remains active during the early stage of CVD step. Apparently, this effect is considerably more pronounced for (111) orientation.

The evolution of the film thickness with CVD step duration on (111) orientation, deduced from TO peak area, is shown in Figure 5. On the same plot, the thickness deduced from interference minimum is reported. The latter value is systematically ~80 nm higher. However, same evolution rate is found from both approaches. We claim that the observed shift is related to the presence of voids, created during carbonization on Si side of 3C-SiC/Si interface. Indeed, voids are present both in (100) and (111) oriented samples. Void's volume is limited by {111} planes. Consequently, for (111) oriented samples, the bottom of the void is parallel to sample surface and creates additional light reflection that contributes to interference pattern.

The cross-sectional SEM observations were performed to verify this hypothesis. An example of the image is shown in Figure 6.

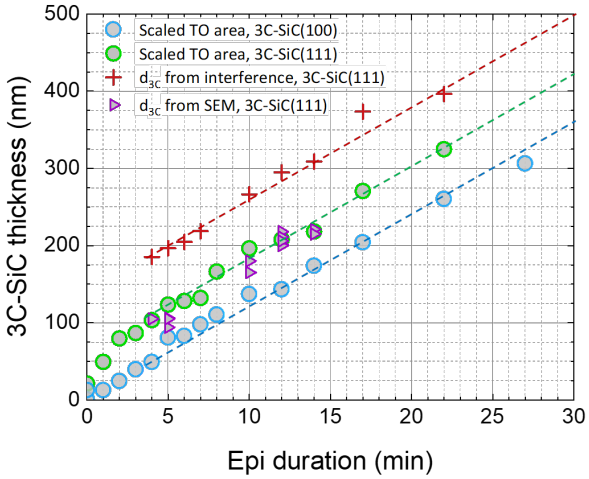

Fig. 5. Evolution of the film thickness determined from TO peak area with CVD step duration for (100) and (111) samples. For (111), the thickness estimation from interference minimum and from SEM cross-sections are also shown.

Unfortunately, the low quality of cross-section preparation (presence of dust/particles on cleaved samples) and of obtained SEM images (limited image sharpness) prevent a systematic quantitative analysis of thickness using SEM. Nevertheless, the 3C-SiC(111) thickness values extracted from usable SEM images and reported on Figure 5 are consistent with TO peak based estimation rather than with the interference related value.

Obviously, the voids have different depths and lateral sizes. Observed 80 nm shift should be considered as an indicator of voids' size and depth distribution. This distribution is in turn correlated with the conditions of carbonization step. We can thus expect that the shift value evolves with carbonization conditions. It could be interesting to seek for correlation between the distribution of the voids' shape and the value of the shift.

Case of DSP substrates. All previously shown results were obtained on samples grown on single side polished (SSP) Si substrates. In this section we show and discuss the modifications that the double side polishing (DSP) of Si substrate brings to the reflection spectrum. We focalize here on comparison between series C and D (3C-SiC(111)) but we verified that similar behavior is also observed for (100) orientation (series E).

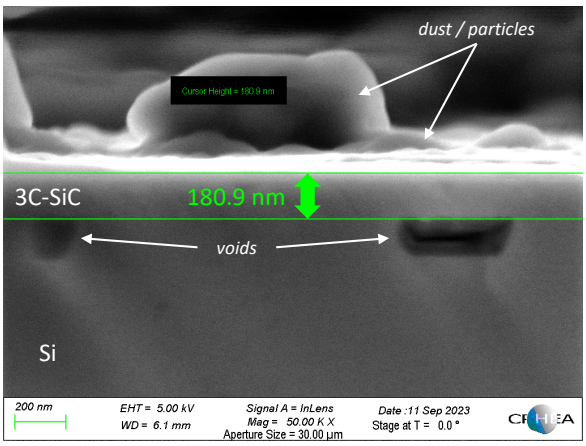

Fig. 6. Example of SEM cross-section of 3C-SiC/Si(111). CVD step duration was 10min.

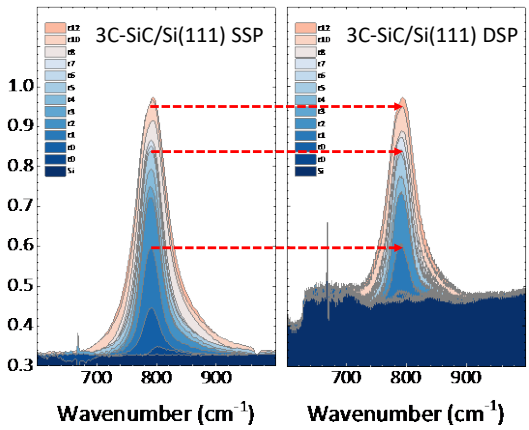

Fig. 7. Comparison of TO spectral region of films grown on (111) oriented SSP and DSP polished Si substrates

The comparison of TO region of IR reflectance spectra of 3C-SiC grown on Si(111) single side and double side polished substrates is shown in Figure 7. Three points are noteworthy: (i) additional short period interference fringes appear, related to the reflection on epiwafer backside. (ii) the reflectance of bare Si wafer, as well as base line of 3C-SiC/Si spectra is higher on DSP than on SSP substrates. (iii) for given CVD step duration, the intensity of the maximum of TO peak is the same on DSP and SSP substrates. Consequently, the TO peak area on DSP sample is lower than on SSP sample grown under same conditions.

The XRD rocking curve measurements of 3C-SiC(111) were performed on series C and D samples. The result is reported in Figure 8. Same peak characteristics (intensity, FWHM, integrated intensity) were systematically found for samples grown under same conditions. It allows us to conclude that despite lower TO peak area same thickness of 3C-SiC was grown on DSP and SSP substrates.

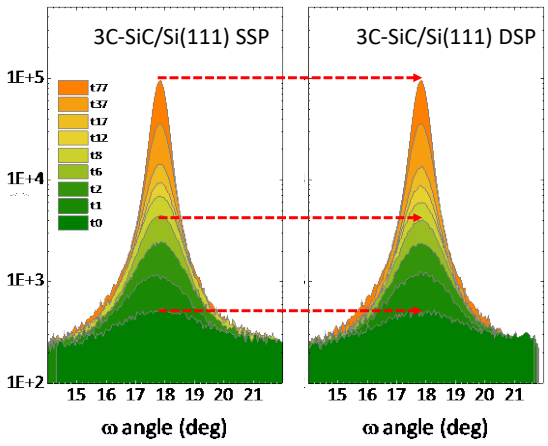

Fig. 8. Comparison of 3C-SiC(111) rocking curve on SSP and DSP Si substrates. CVD step duration from 0 (carbonization only) to 77 minutes.

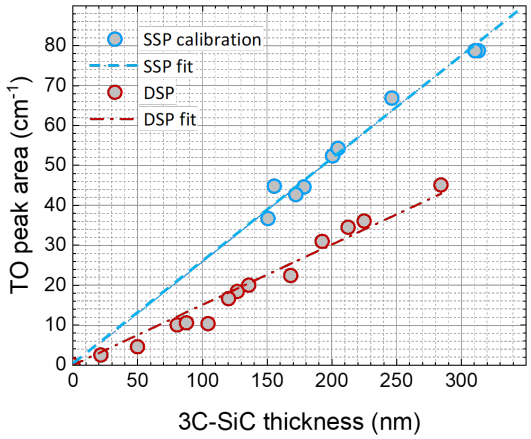

Fig. 9. Thickness dependance of TO peak area for films grown on SSP and DSP substrates.

Figure 9 shows the evolution of the TO peak area with epilayer thickness on SSP and DSP samples. For SSP samples, the points measured on 3C-SiC(100), series A and B, are reported (see "Scaling factor" section). For DSP samples, the thickness values were taken from 3C-SiC(111) SSP series. The scaling factor $K=6.62\pm0.20$ nm/cm^{-1} is higher and the quality of the linear regression ($R^2=0.967$) is slightly lower than that on SSP samples ($R^2=0.974$), but it remains satisfactory. To achieve a better accuracy would require a more advanced approach that takes into account the reflectivity offset related to DSP preparation.

Conclusion

We performed a systematic experimental study of the evolution of the 3C-SiC TO spectral feature with the duration of CVD growth. The TO peak area parameter was defined. For 3C-SiC films grown on SSP Si wafers, we demonstrated that TO peak area can be easily scaled in terms of thickness. Same scaling factor was obtained for (100) and (111) oriented films. It was independent on Si substrate doping for low and medium doping range.

Additionally, the study brought into evidence that for 3C-SiC(111) the deposition rate in the initial stage of growth is higher than for 3C-SiC(100). Also, the 3C-SiC(111) thickness determination from interference features (fringes, minima) can be affected by systematic shift related to the presence of interfacial voids. This effect is not visible on (100) orientation. Finally, we demonstrated that for 3C-SiC films grown on DSP Si substrates, a higher value of scaling factor is found.

Acknowledgments

The authors would like to express their gratitude to Mr. Thierry Bourgoin for continuous technical supervision of growth equipment. Corresponding author thanks Mr. Antoni Zielinski for his motivating contribution to the study. This work has been supported by the European project PicoGeo (Call: H2020-FETOPEN-2018-2020, Proposal number: 863220).

References

[1] Kermany et al. Appl. Phys. Lett. 104 (2014) 081901.
[2] Yannick S. Klaß et al, Appl. Phys. Lett. 121 (2022) 083501.
[3] Portail et al. J. Appl. Phys. 105 (2009) 083505.
[4] C. J. Mogab, J. Electrochem. Soc., Vol. 120 (1973) 932.
[5] G. Ferro et al. Thin Solid Films 278 (1996) 22-27.
[6] J. Camassel, J. Pernot, H.Y.Wang, H. Peyre, Phys. Stat. Sol. (A) 195 (2003) 38.
[7] A. Leycuras, Mater. Sci. Forum, 338–342 (2000) 241.