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Determination of the optical bandgap and disorder energies of thin amorphous SiC and AlN films produced by radio frequency magnetron sputtering

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Abstract. Amorphous aluminum nitrite and silicon carbide (*a*-AlN and *a*-SiC) thin films were prepared by radio frequency magnetron sputtering. Due to the deposition method and production conditions the deposited films grown in amorphous state. We systematically measure the optical bandgap through optical transmission spectroscopy and its change with a cumulative thermal annealing. The results show a linear relation between the Tauc-gap and the Tauc-slope for both AlN and SiC films, which can be explained analytically from the existence of an Urbach focus, and therefore can be used to determine the Urbach focus or to ensure the correct usage of the bandgap determination methods.

1. Introduction

Amorphous and crystalline thin films of the wide bandgap materials AlN or SiC are of increasing interest in research and development [1-4], not only because properties like their higher breakdown voltage and thermal conductivity in contrast to usual semiconductors like GaAs and Si [5], but due to their potential applications in optics, *e.g.* amorphous SiC thin films have been used as coatings for extreme UV optics due to its high reflectivity in the UV region [3]. Also, amorphous AlN doped with rare earths has applications for micro wave guides and lasers [4]. In summary there are plenty of potential applications to develop for these materials, and therefore a good understanding of their optical properties is necessary.

In the last decades different methods and/or representations of the absorption coefficient have been used to determine the optical bandgap of *a*-AlN thin films and therefore several values of the optical bandgap have been given [6-10]. The differences on these values were attributed to the different structures of the material since the films are amorphous and to the deposition methods. We attribute those differences not only to the process conditions or structure but to the misusage of the bandgap

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determination methods, since different regions of the absorption coefficient were used to determine the optical bandgap assuming them as the fundamental absorption. We propose a simple criteria to ensure the correct measure of the optical bandgap from the fundamental absorption.

We present the variation of the absorption coefficient of *a*-AlN and *a*-SiC thin films versus annealing temperatures measured by means of optical transmission measurements (fig. 1). From which by using a proper representation of the absorption coefficient the optical bandgap can be obtained commonly by the intercept of a linear extrapolation with the photon energy axis. Also we measure structural parameters like the Tauc-slope and Urbach-slope (also known as Urbach parameter) and relate them to the corresponding optical bandgap. The Urbach-focus of the *a*-AlN is found to be at 6.002 ± 0.015 eV in excellent agreement with the value of the optical bandgap of crystalline AlN (*c*-AlN) [11]. The Urbach focus of the *a*-SiC is found to be at 3.164 ± 0.063 eV.

2. Experimental details

The studied films were grown on quartz and CaF_2 substrates by radio frequency magnetron sputtering from highly pure SiC and AlN targets of 51 mm diameter in an argon and nitrogen process atmosphere respectively. The dominating impurities are nitrogen with a concentration below 10 ppm wt for the SiC target and oxygen (90 ppm wt) for the AlN target. The substrates where hold down at 10°C with a constant water flux by a cooling system to ensure an amorphous lattice in the film.

The annealing treatments took place in a quartz tube inside an oven tube with three heating stages which can be heated up to 1200 °C. The quartz tube was evacuated down to 4×10^{-5} mbar and then a constant argon flux raises the pressure up to $\sim4\times10^{-4}$ mbar. After the operating temperature was reached, the quartz tube with the samples under treatment was moved rapidly inside the oven (shock tempering). The annealing time for each annealing step was 15 minutes and the same samples were used for the next annealing steps (isochronical annealing).

The *a*-SiC and *a*-AlN films were studied by optical transmission spectroscopy at room temperature using a double beam photo-spectrometer model Lambda 2 UV/VIS/NIR of Perkin Elmer in the range of 190-1100 nm with a spectral resolution of 1 nm. Absorption coefficients up to 15×10^4 cm^{-1} were recorded. The substrates were also measured to be taken into account for further calculations.

3. Results and Discussion

The calculation of the absorption coefficient from the transmission spectrum was performed using a modified Swanepoel's method [9][10][12][13] which consist in a fit using the transmission spectra without interference fringes T_α and the measured transmission spectrum itself T. The T_α curve is calculated from the envelopes that are constructed using the extremes from the T curve. Also, the refractive index of the substrates and their change with the annealing treatments were considered. This method gives the thickness, refractive index and absorption coefficient with a good accuracy and can be applied to transmission spectrums with a low interference pattern typical of films with a thickness around 450 nm in our case [9][10][12][14]. According to this method the films had a thickness around 350 nm and a small variation was noted after the films were annealed. The optical bandgap can be obtained from the Tauc-plot analysis commonly used in similar studies.

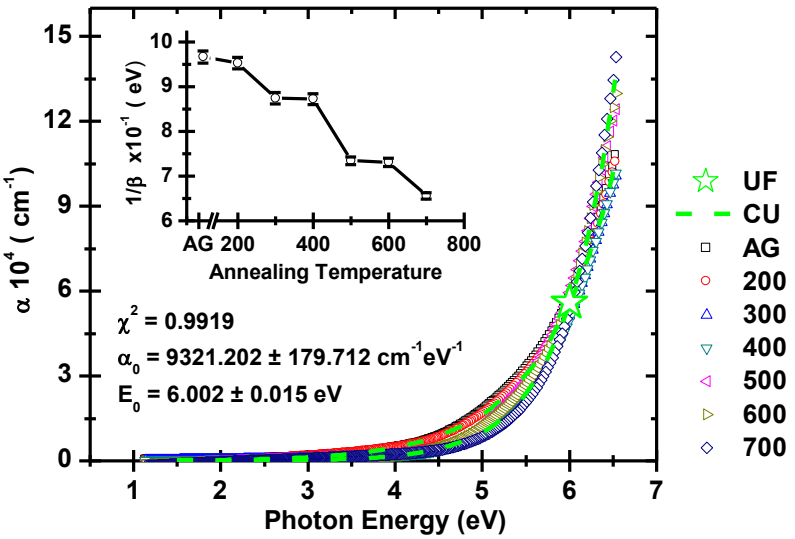

Figure 1. Absorption coefficient of pure *a*-AlN at different annealing temperatures (°C). The green dashed lines are a fit using the Cauchy-Urbach model. The point denoted by a green star is the Urbach focus. The inset graph shows the change of the Urbach-slope with the annealing treatment. AG stands for as-grown.

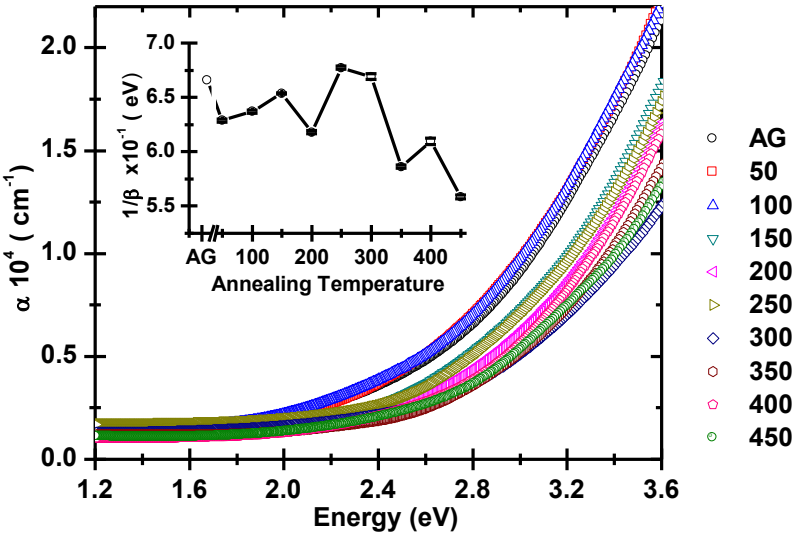

Figure 2. Absorption coefficient of pure *a*-SiC at different annealing temperatures. In this case, no Urbach focus was observed directly. Inset graph shows the change of the Urbach-slope with the annealing treatment.

It is easily shown from the Urbach-rule (eq. 1) that the Urbach-focus value corresponds to the parameter $E_f = E_0$ and the corresponding ordinate value is $\alpha_f = \alpha_0$ by assuming that only a change in β occurs when a sample is annealed or a change in the structure occurs by other means.

$$\alpha = \alpha_0 \exp[\beta(E - E_0)] \tag{1}$$

Motivated by the Urbach-rule, another commonly used model in similar and ellipsometric studies [7] give in the same way a definition of Urbach-focus (eq. 2). This model is known as Cauchy-Urbach model, and following the above notation the corresponding Urbach focus is defined by $E_f = E_0$ and $\alpha_f = \alpha_0 E_0$. Both models denote the same focus.

$$\alpha = \alpha_0 E \exp[\beta(E - E_0)] \tag{2}$$

It is well establish, that the optical bandgap is broadened by the structural and vibrational disorder on the lattice. Then it seems reasonable to calculate the optical bandgap of an amorphous material by subtracting the energy broadening by the disorder from the energy gap between the mobility edges [15-18]. In principle the energy gap between the mobility edges or the bandgap in the absence of static disorder should match the one of the material in the crystalline case. However we do not intend to enforce this constant but to obtain it directly from the experimental results of the studied amorphous materials.

Our election of the Urbach-focus as the bandgap in absence of static disorder is suggested by the experimental results in the case of AlN and SiC samples as we will show in the next paragraphs. The Urbach-focus value can be obtained in two different ways. First it can be determined directly from the absorption coefficient data through a proper fit using the Cauchy-Urbach model or the Urbach rule. It is important to note that in order to determine the three parameters α_0, E_0 and β a global fit sharing the parameters α_0 and E_0 must be performed in the case of annealed samples. This implies that the parameter E_0 is a constant that does not depend on the structure change due to the annealing treatment. Second, the Urbach-focus can be also determined from a less direct but still proper linear regression, which will be shown also in the next paragraphs.

To make the fit first note that in the Urbach rule written in logarithm scale we have a linear equation (see eq. 4), whose intercept is describe by $\ln(\alpha_0) - \beta E_0$ and slope by β. Thus from a single measurement of the absorption coefficient the Urbach slope is well defined but the rest of parameters are not in the sense that they can have any value satisfying the intercept relation. The same happens with the Cauchy-Urbach model.

$$\ln(\alpha) = \ln(\alpha_0) - \beta E_0 + \beta E \tag{4}$$

Therefore, from several measurements of the absorption coefficient of a material but with different disorder degrees, a change in the slope is expected and the Urbach-focus is defined by the intersection

of the curves. This effect is observed in the figure 1 for *a*-AlN films annealed at different temperatures. In the case of the *a*-SiC shown in the figure 2 it seems that there is a not well defined Urbach-focus.

The other way to obtain the Urbach-focus is trough the fundamental absorption representation. Let us generalize it through the equation 5 shown below. Where for $r = 2$ we have the Tauc's representation and for $r = 1/2$ we have the $(\alpha E)^2$ representation.

$$\alpha = B(E - E_r)^r / E \tag{5}$$

Then by taking into account the Urbach-focus in the equation 5 and solving for the bandgap E_r we obtain the equation 6. It is important to note that this equation works for any exponent r and that the Urbach-focus can be determined form its intercept. The equation 6 is also giving energy units to another well known parameter that represents the disorder in the lattice, the Tauc slope [16] *i.e.* for $r = 2$.

$$E_r = E_0 - (\alpha_f E_f)^{1/r} \, 1/B^{1/r} \tag{6}$$

Therefore in order to determine the Urbach-focus it is necessary to plot the Tauc-gap versus the Tauc-slope and fit the equation 6, see figure 3. In this way if the Tauc-gap is being determined from the fundamental absorption it must follow the equation 6, *i.e.* the region of the absorption coefficient where the Tauc-slope is increasing with the reduction of the disorder [16].

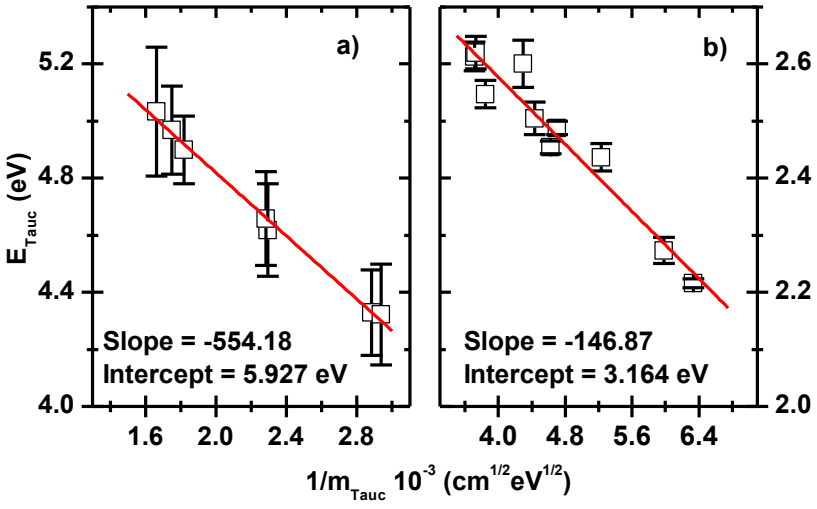

Figure 3. Tauc-gap versus the inverse of the Tauc-slope for *a*-AlN (a) and *a*-SiC (b), showing a well defined linear relation corresponding to the equation 6.

This result clears all doubt of which region of the absorption coefficient should be used to determine the optical bandgap through the selected representation if the material shows an Urbach-focus and is a

constant under structural changes on the lattice. This is not the case for the SiC that in amorphous state may show different pseudo hybridization states that change the bandgap and the structure and therefore the Urbach-focus varies with the annealing treatments, see figure 2. For the case of *a*-SiC the only way to obtain an average value of the Urbach focus would be through the equation 6, see figure 3, even if no apparent focus is observed in the figure 2 since it is changing for different annealing temperatures.

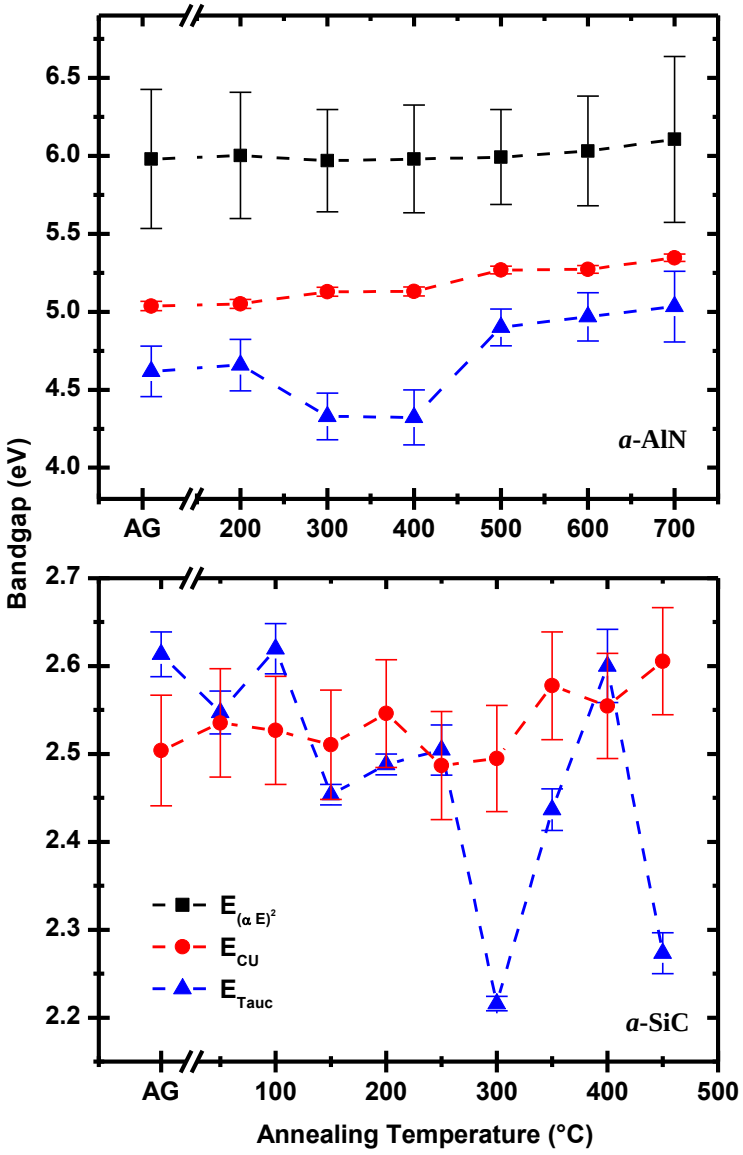

Figure 4. Tauc-gap (blue triangles) for the *a*-AlN (above) and *a*-SiC (below). The $(\alpha E)^2$-gap is shown for comparison in the AlN case. Also the difference between the Urbach focus and the Urbach-slope is shown (red circles) for each sample.

4. Conclusions

Another method besides a fit using the Urbach rule or the Cauchy-Urbach models to determine the Urbach-focus of a material using the Tauc-gap and the Tauc-slope was presented. The experimental results show that the Urbach-focus of amorphous AlN and SiC materials can be used as a constant that represents the gap between the mobility band edges. Also, it can be seen that the chosen representation of the fundamental absorption changes the representation of the energy loss by the disorder through the equation 6. In this sense, the search for a proper representation of the fundamental absorption to determine the optical bandgap should look into a proper representation of the topological disorder and its influence on the fundamental absorption of a material. A candidate to fit as a parameter that represents the topological disorder could be the Urbach-slope [12] since the difference between the Urbach-focus and the Urbach-slope give a value closer to the bandgap and carries the behavior of the disorder reduction, see figure 4.

Acknowledgements

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