

CaF₂ for DUV lens fabrication: Basic material properties and dynamic light–matter interaction

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ABSTRACT

Lens fabrication for the short wavelengths of the DUV spectral range requires the replacement of glasses, by the crystalline material CaF₂. We review mechanism for the interaction of CaF₂ with electromagnetic radiation, especially at wavelengths of 193 nm and 157 nm. In the ideal material an absorption process can occur only via a two photon process where charges are separated and an electron–hole pair is created in the material. These excited charges can localize as charge centers or as a localized excitonic state, a bound F[−]-H⁺-pair. At room temperature all charge centers should recombine within a few pico seconds and no long time change of the optical material properties should be observable. In the real material not only charge center formation but also the stabilization of these charge centers at room temperature due to impurities is identified as a key for the understanding of a radiation induced change of optical material properties.

Keywords: optical microlithography, ionic crystal, CaF₂, excitonic bound state, color center, self trapped exciton

1. INTRODUCTION

When structuring semiconductors using a microlithographic process the quality of the resulting structures crucially depends on the optical imaging system. The wiring plan of the chip which is on the mask has to be accurately imaged on the photo-resist which is the radiation sensitive layer on the silicon wafer. The wavelengths for structuring are dictated by available excimer laser sources. For 193 nm this is a ArF-laser and for 157 nm a F₂-laser is used. Already at 193 nm but even more clearly at 157 nm even synthetically produced fused silica glasses show non satisfying properties with respect to radiation stability and a too large absorption. In addition the fused silica applied in 193 nm lens systems needs to be chromatically corrected by a second material. This material is the crystalline material CaF₂. It has a large band gap of 11.8 eV and can be produced as large single crystals which are nearly free of internal mechanical stress. It is further very stable under high radiation doses. The small spatial dispersion induced optical anisotropy at 157 nm¹ is microscopically well understood² and can be compensated by lens design by using lenses of oriented crystals with light propagating mainly along the [111] and [100] direction, respectively.

Currently material is available which fulfills the specifications for 193nm and 157 nm optics. For 193 nm applications CaF₂ optical elements are mainly applied close to the laser light source, where high radiation doses are present. In the current work we investigate possible mechanism for radiation induced change of optical material properties under extreme radiation intensities.

The paper is organized as follows: In sec. 2 we define an ideal material where radiation can only be absorbed via two photon processes. This results in a separation of charges which relax to F[−]-H⁺-pairs. The next sec. 3 shortly reviews the charge center physics occurring in CaF₂. However at room temperature the lifetime of charge centers should not exceed a time of a few ps. This situation may change in a real material sec. 4 where charge centers can be stabilized due to the existence of point defects. The impact on the material development of large crystals of CaF₂ is summarized in the conclusion sec. 5.

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2. IDEAL MATERIAL

Let us for a moment define an ideal material. This ideal material has a complete translation symmetry and neither point defects nor grain boundaries. The only possible way to make an excitation in such a material goes via a two photon process.³ To illustrate this we have plotted in Fig. 1 the schematic optical density of states at the band edge. The exciton resonance at 11.2 eV and the band edge at 11.8 eV are shown. These energies are compared with the single and double photon energies of radiation of 157 nm (7.9 eV) and 193 nm (6.4 eV) wavelength respectively. Under intense radiation a two photon process occurs with a small but finite probability which increases quadratically with increasing radiation intensity. In Fig. 2 we show the optical density of states from⁴ and plot twice the single photon energy for 157 nm and 193 nm excitation, respectively. The measured spectrum compares well with recent density functional calculation results.⁵ The two photon process creates a free electron-hole pair in the one particle continuum. This pair will eventually relax and find a two particle bound state, the (delocalized) exciton.⁶

When further localizing the electron-hole pair a self trapping mechanism sets in. The self trapping acts via a lattice distortion. Here the gain in energy due to the lattice distortion exceeds by far the loss in energy due to localization of the electron-hole pair. This is schematically shown in Fig. 3. It leads to a fluorescence at a wavelength of 278 nm. The corresponding self-trapped-state is called the F^-H^+ -pair.^{7,8} It consists on one hand of an F^- ion which is moved out of its equilibrium position leaving a vacancy behind. In this vacancy an electron is localized forming an F^- -electron-charge center. On the other hand the F^-H^+ -pair consists of the F^- ion being shifted to a neighboring Fluor site where it forms a F_2^- together with the Fluor ion already located there. The excess positive charge, the hole, is trapped in this position by forming an F_2^+ state. In this way an H^+ -hole-charge center is created. The F^-H^+ -pair is therefore the localization of an electron-hole pair in the form of an F^- -charge center and a H^+ -charge center which compensate their charges by being located on neighboring lattice sites. In section 3 we discuss the physics of these charge centers in more detail. At room temperature such an F^-H^+ -pair recombines with the relative long time of a micro second^{7,9,10} which is however much shorter than any timescale in the lithographic process and should therefore have no impact on the optical properties of CaF_2 at 193 nm and 157 nm respectively.

2.1. Equilibrium concentration of defects at room temperature

In this sub-chapter we outline that even the above defined ideal crystal has an equilibrium concentration of defects at room temperature. As an example we take the fluor on an interstitial lattice position leaving a fluor vacancy behind. We know from numerous measurements, especially of the conductivity, that the fluor sub-lattice melts at approximately 1450 K.¹¹ This is the temperature where the ion conductivity of F^- ions sets in. At this temperature the average thermal energy exceeds the depth of the potential well which traps the fluor on its lattice position. The depth of this well is therefore $k_B 1500$ K, where k_B is the Boltzmann constant. Which means we have to employ an energy of $k_B 1500$ K ≈ 0.13 eV in order to remove a fluor ion out of its lattice position. On the other hand we know that the thermal distribution of this fluor vacancies has to follow a Maxwell-Boltzmann distribution as a function of temperature.

$$N = N_0 e^{-\frac{\Delta E}{k_B T}} \quad (1)$$

This means that at room temperature we have in thermodynamic equilibrium a number of $N/N_0 \approx e^{-5} \approx 0.007 = 0.7$ % of fluor ions which are moved out of its equilibrium position. These defects can act as precursors for charge center formation.

3. CHARGE CENTERS

The two charge centers which are mostly discussed in CaF_2 are the F^- -center and the H^+ -center.¹² The F^- -center is an electron which is trapped in a fluor vacancy. The surrounding lattice answers to this with a lattice distortion. The H^+ -center (or v_H -center) is created by an excess fluor ion. This excess fluor ion goes onto the lattice site where already a fluor ion is present and both together form an F_2^- molecule. This F_2^- molecule is identical to the localization of an effectively positive charge. From experiments it is known that the F^- -center has a broad absorption at 3.1 eV (400 nm) with a width of 1.2 eV and that the H^+ -center shows an absorption of similar width at 4.1 eV (305 nm).

We can understand charge centers as a quasi "hydrogen atom" where an excess charge (either an electron or a hole) is trapped due to the coulomb force accompanied by a lattice defect. Such a simplistic picture does not take into account the particular symmetry of a charge center with respect to the surrounding lattice symmetry. However it allows to estimate some important quantities.

$$E_n = -\frac{me^4}{2\epsilon_0^2\epsilon^2\hbar^2} \frac{1}{n_l^2} = -13.6eV \frac{m}{m_e} \frac{1}{\epsilon^2} \frac{1}{n_l^2} \quad (2)$$

where n_l is the number of the level, e is the electron charge, m the effective mass of the charge, m_e the electron mass, $\epsilon = 6.76$ the static dielectric constant of CaF_2 and \hbar the Planck constant. The absorption line at 3.1 eV for the F^- -center and at 4.1 eV for the H^+ -center are the excitation from the ground state ($n=1$) to the first excited state ($n=2$) of a charge in a Coulomb potential ($1/1^2 - 1/2^2 = 3/4$). That means we can estimate the effective mass of the charges as follows:

$$m_{H^+} = 4.1 (6.76)^2 \frac{4}{3} \frac{1}{13.6} = 18.4 m_e \quad (3)$$

$$m_{F^-} = 3.1 (6.76)^2 \frac{4}{3} \frac{1}{13.6} = 13.9 m_e \quad (4)$$

That means that the effective mass of the trapped electron is 13.9 times the electron mass and the effective mass of the trapped hole is 18.4 times the electron mass.

We can now estimate the integrated cross section in analogy to the hydrogen atom. This results in¹³

$$\int d\nu \sigma(\nu) = \frac{e^2}{4\epsilon_0\epsilon m c} 0.416 \quad (5)$$

For the charge centers in CaF_2 this results in

$$\begin{aligned} F^- : \int d\nu \sigma(\nu) &= 8.8 \cdot 10^{-3} \frac{m^2}{s} \\ H^+ : \int d\nu \sigma(\nu) &= 11.8 \cdot 10^{-3} \frac{m^2}{s} \end{aligned} \quad (6)$$

This is an upper boundary for the integrated cross section of charge centers. The values allow to estimate the concentration of charge centers from a given absorption spectrum. It is important to note that the total integrated cross section is much larger than cross sections of direct ionic excitations.

Further charge centers which are discussed are for example the ν_k -center. The ν_k -center is similar to the H^+ -center with the difference that the F_2^- molecule is created out of 2 fluor ions which are only slightly shifted from there original positions. Further charge centers are the M-center with an absorption around 520 nm, created out of two F^- -centers and the R-center with an absorption around 650 nm, created out of three F^- -centers. For a review see e.g.¹² In an ideal crystal charge centers become mobile above 190 K. That means that there is a very high probability that an F^- center finds an H^+ center and recombines very fast. Therefore the ideal crystal does not allow for a long term stable change of its optical properties.

4. REAL MATERIAL

In the real material defects are present. These can be either point defects like impurity atoms or vacancies or defects of higher dimension like grain boundaries. Local impurity atoms can have direct electronic transitions which are known e.g. for O^{2-14} . In the material currently produced for microlithographic purposes the concentration of impurity ions is below the ppm level. Therefore — at least at room temperature — direct electronic transitions should be suppressed to such a low level, that no direct absorption is observable.

Charge centers, however, have very large cross sections (see sec. 3). Therefore the main impact on the optical properties by defects is that they are able to stabilize charge centers at room temperature. If charge centers are trapped their diffusion motion is hindered and they are unable to recombine and annihilate each other. The

trapping of charge centers can occur due to two mechanisms. The first one (i) is a charge compensation. For example an F^- -center with a negative charge is trapped by an additional positive charge which can be a three fold positively charged ion on a Ca site. The second mechanism (ii) is due to a lattice distortion. A charge center can be accompanied by a lattice distortion of an area of typically 20-50 atomic positions surrounding the excess charge. Such a lattice deformation can be preferred by a defect and therefore trap a charge center. Examples for this physics can be found in,¹⁵ specifically for Pb doped CaF_2 ,¹⁶ Sr doped material¹⁷ and Na doped CaF_2 .¹⁸ Also pairs of defect ions (e.g. Na^+ , Ce^{3+}) can compensate each others charge leading only to a short range dipolar field but can lead to a stable lattice distortion.^{19,20}

5. CONCLUSION

In the present paper we argue that a long time change of optical properties under intense radiation is mainly caused by the stabilization of charge centers due to material defects. In the absence of defects all charge centers, which are produced by intense radiation via two photon processes will at room temperature recombine within a timescale of microseconds. This recombination is hindered by trapping of charge centers on defects like e.g. impurity ions.

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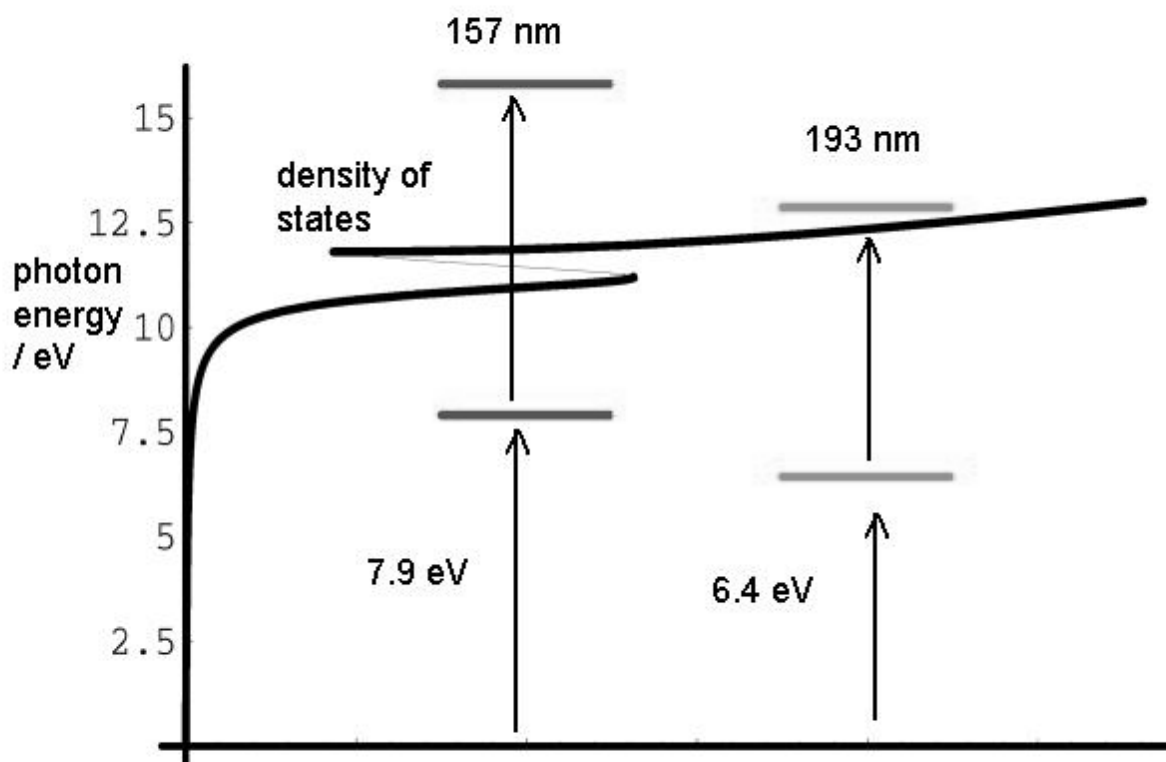


Figure 1. Schematic plot of the optical density of states. The band gap is 11.8 eV and the exciton resonance is at 11.2 eV. In comparison to the band gap the photon energy of radiation with 157 nm and with 193 nm wavelength is shown. A two photon process can in maximum excite an energy of twice a single photon.

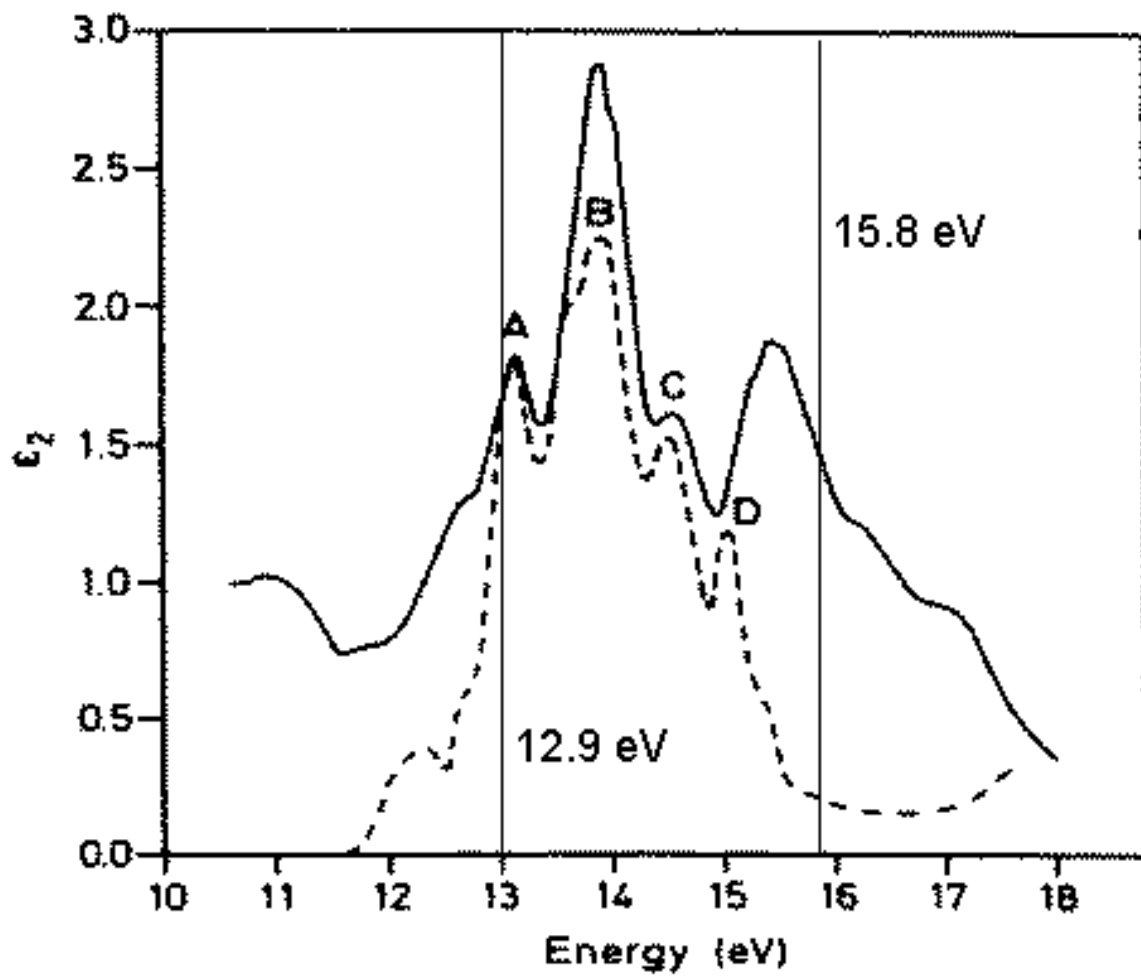


Figure 2. According to⁴ the optical density of states measured with ellipsometry at a synchrotron is shown (solid line). The measured optical density of states compares well to density functional calculations⁵.

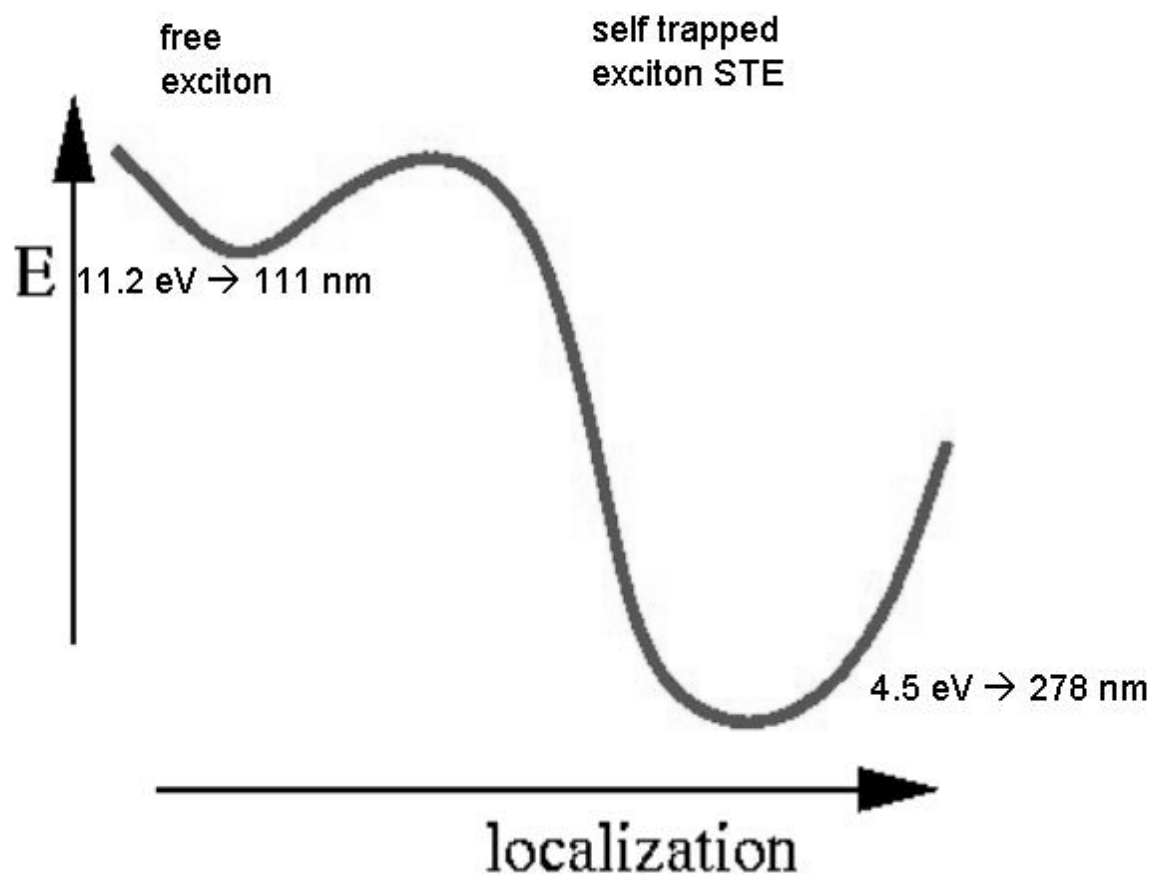


Figure 3. Schematic plot of the localization of the electron hole pair which leads to a self-trapped state, the F^-H^+ -pair. The F^-H^+ -pair is the origin of a fluorescence occurring at 278 nm.

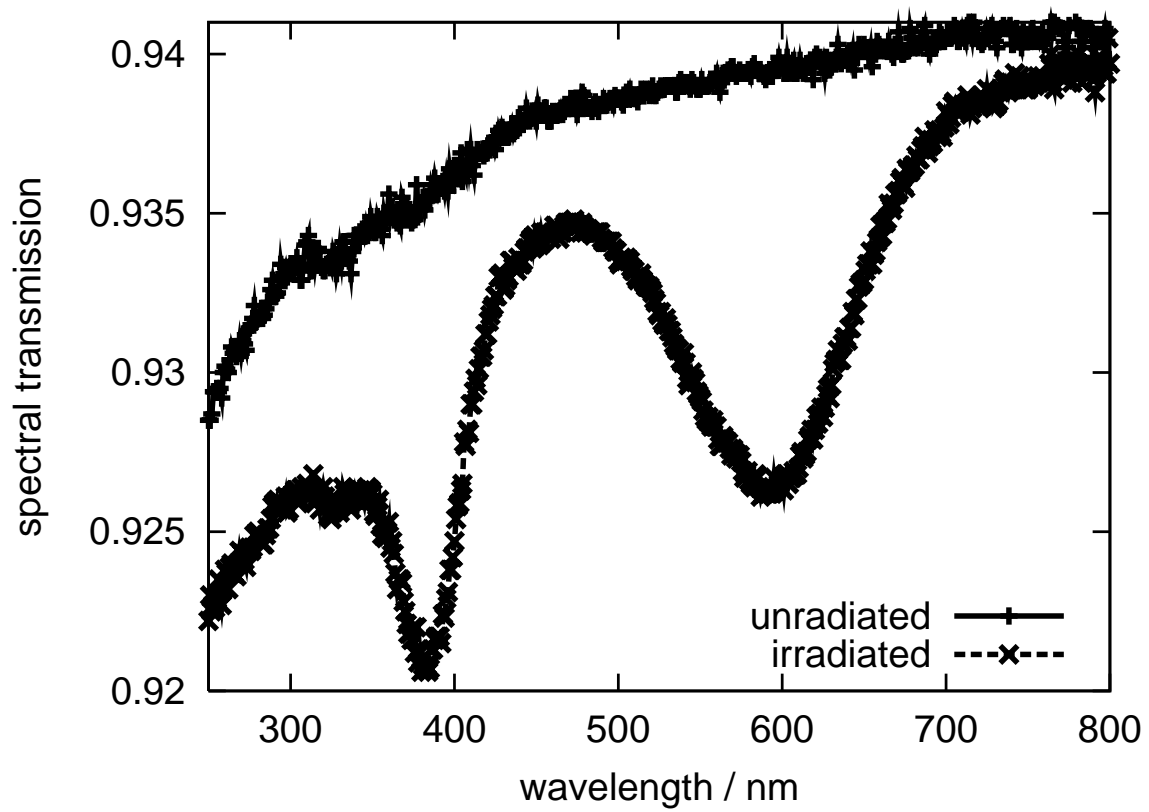


Figure 4. Spectral transmission of a R&D sample of CaF_2 before and after intense laser radiation with 193 nm laser light. At the wavelength of F^- -center (around 400 nm) and of M-center (around 600 nm) additional absorption occurs. The sample thickness was 100 mm.