Vacuum ultraviolet emission bands of LiLuF$_4$:Tb^{3+} crystals in the spectral range from 157 to 200 nm

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Abstract

The absorbance of most carbonated polymeric materials just has the right value of ~ 0.1–0.4 μm^{-1} for lithographic imaging in the spectral region from 170 to 193 nm. Also, the resist out-gassing is less in this spectral region in comparison to 157 nm. As a consequence the development of vacuum ultraviolet (VUV) light sources for lithographic applications at wavelengths between 157 and 193 nm should be seriously taken into consideration. The experimental results of this work suggest that the LiLuF$_4$:Tb^{3+} crystal can be considered as a candidate towards the development of new VUV light sources for lithographic applications at wavelengths between 157 and 193 nm. The 4f$^8\leftrightarrow$4f^{7}5d dipole allowed transitions of the Tb^{3+} ions in LiLuF$_4$ crystal hosts, were investigated with VUV absorption spectroscopy and laser-induced fluorescence using as the excitation source the molecular fluorine laser at 157 nm. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

High-resolution lithography is required for next generation memory and logic products, and 157 nm lithography is on the road-map to achieve sub-100 nm resolution. However, there are problems related with the application of 157 nm lithography. The most serious ones being (a) choosing polymeric materials having the right value of the absorption coefficient at 157 nm and limited out-gassing, and (b) selecting optical material for the projection system without compactness. Indeed, the high value of the absorption coefficient of the polymeric materials in the vacuum ultraviolet (VUV) sources, ranging from 10^4 to 10^6 cm^{-1}, imposes restrictions on the selection of the resists for 157 nm photolithography, and hence demands high-purity materials and defect-free thin films [1]. That can be explained by the fact that, for most of the organic materials, the density of the excited electronic

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states, dissociative or bound, around 7.8 eV (157 nm) is high enough, suggesting a large value for the absorption coefficient at this wavelength. On the contrary, the absorbencies of various carbonated polymeric materials at wavelengths longer than 170 nm, might just have the right value of ~ 0.1–0.4 μm^{-1} for lithographic imaging, mainly due to the fact that for all the organic molecules, the dissociative excited electronic states of the small radicals occupy the energy range above 6.2 eV (200 nm). In this case the energy position of the first excited states of the C–C bond and the basic diatomic radicals depends on the chemical structure of the polymeric material, allowing therefore large variations of the absorbencies (and hence ''tuning''), in a narrow frequency range. Taking into consideration that potential VUV resistive materials indicate a sharp drop of the absorption coefficient for wavelengths longer than 170 nm [2], the development of VUV light sources for lithographic applications at wavelengths between 157 and 193 nm should be seriously taken into consideration [3]. The VUV emission and absorption spectroscopic characteristics of the rare earth (RE) ions, activated in the wide band gap of fluoride dielectric crystals, suggest that they can be used for a variety of applications, such as generation of VUV coherent or incoherent light. These applications are depending on the basic physical properties regarding the structure of the levels of the $4f^{n-1}5d$ electronic configurations of the trivalent RE ion and the strength of the interconfigurational $4f^{n-1}5d \rightarrow 4f^n$ transitions. These transitions, with strong Frank–Condon factors, are responsible for the broad-band absorption and emission spectra. Besides it, research on wide band gap dielectric crystals is stimulated by the following reason: Optical quality of materials used for VUV lithographic projection systems degraded constantly under VUV radiation. Recently it was found that even CaF_2 is subject to refractive index variations under prolonged VUV irradiation. Wide band gap fluoride dielectric crystals, such as $LiCaAlF_6$, could be considered as the alternative choice to CaF_2 for 157 nm photolithography [4] despite the fact that they crystallize at different symmetry groups than cubic. In this case refractive index stability could be achieved by separating different polarizations following conic refraction. In this communication, we report on the interconfigurational $4f^7 5d \rightarrow 4f^8$ VUV fluorescence of the Tb^{3+} ion in the $LiLuF_4$ single crystal host, as it is excited with the laser radiation from the fluorine pulse discharge, molecular laser at 157.6 nm. The energy position of the levels of the Tb^{3+} ions in the VUV was determined using VUV absorption spectroscopy. The experimental results suggest that the $LiLuF_4:Tb^{3+}$ crystal can be used as new VUV light source for lithographic applications at wavelengths between 157 and 193 nm where resists have the correct absorption for single layer imaging.

2. Experimental

The $LiLuF:Tb^{3+}$ monocrystals, were grown in carbon crucibles, with the Bridgman–Stockbarger method. The concentration of the Tb^{3+} ions in the samples was from 0.01 at.% to 0.1 at.%. The samples were optically polished disks, having the diameter of 5 mm and their thickness was 0.5 mm. The experimental apparatus for obtaining the excitation spectrum consists of the F_2 molecular laser as a pumping source, the vacuum chamber where the crystal samples were placed, the focusing optics and the detection electronics and it has been described previously [4]. The laser-pumping source was a laboratory build F_2 molecular laser, which delivers 12 mJ per pulse, and the pulse width was 12 ns at FWHM. Only 1 mJ was used to excite the crystal sample. The line width of the corresponding F_2

laser transition was found to be within the limit of the resolution of the monochromator ∼0.1 nm. The direction of the laser beam was at right angles to the optical axis of the crystal. The fluorescence light was detected along the optical axis as well. In order to reduce the emission light from the laser discharge, a band-pass filter (23% transmission at 157.6 nm, 26 nm bandwidth) was placed in front of the crystal sample. The detection system consisted of a 0.2 m VUV monochromator, a solar blind photomultiplier and a Box–Car integrator interfaced to a personal computer. The absorption spectrum in the VUV was recorded using a hydrogen lamp operating in a longitudinal stabilized discharge mode. The high stability of the discharge, results in good signal-to-noise ratio, (better than 2000). The optical path of the exciting and the fluorescent light was under vacuum at 10^{-5} mbar background pressure, using vacuum lines from stainless steel 316.

3. Results and discussion

The absorption spectrum of the $LiLuF_4$:Tb^{3+} crystal in the spectral range from 150 to 200 nm is shown in Fig. 1. The absorption peaks were assigned to the $4f^8 \rightarrow 4f^7(^8S)5d$ dipole transitions of the Tb^{3+} ion. The electric crystal field splits all the levels of single and mixed electronic configurations of the Tb^{3+} ions. The number and the spacing of the components depend on the symmetry and the intensity of the crystal field. According to Szczurek and Schlesinger [5], the $4f^7$ electronic configuration of the Tb^{3+} ion is half filled, and the lower energy level of the $4f^7 5d$ electronic configuration is the $^8S_{7/2}$ one, which has zero total angular momentum. Therefore in a pure *L–S* coupling the 5d electron does not interact with the $4f^7$ shell. The interaction is taking place only through the crystal field. In this aspect the Tb^{3+} ion is rather similar to the Ce^{3+} one, though the last one in the 5d electronic configuration has an empty 4f shell. As a result the low energy part of the absorption spectrum of the Tb^{3+} ions in the $4f^7 5d$ electronic configuration should be quite similar to that of Ce^{3+} one. The absorption spectra of $LiLuF_4$:Tb^{3+} in the spectral range from 140 to 220 nm consists of a band displaying similar structure to the spectrum of Ce^{3+} ions in crystal field in the spectral range from 180 to 320 nm. The separation between the extreme lines in the spectra are about
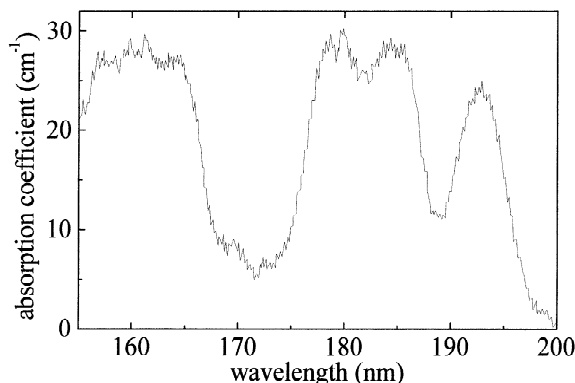

Fig. 1. VUV absorption spectrum of the $LiLuF_4$:Tb^{3+} crystal. The concentration of the Tb^{3+} ion in the $LiLuF_4$ crystal was 0.1 at.% and the crystal sample was 0.5 mm thick.

20600 cm^{-1} for terbium and about 21600 cm^{-1} for cerium. This experimental evidence supports the argument that in both cases the lowest energy level system in the 4f^{n-1}5d electronic configuration is formed through the interaction between the 5d electron and the crystal field. Following this argument and taking into consideration that spherical symmetry is partially restored [6], the 4f^7(^{8}S)5d electronic configuration consists of two terms, the ^{9}D and the ^{7}D one, and only the ^{7}D$_5$ is populated through the electric dipole transitions from the ^{7}F$_6$ ground level of the 4f^8 electronic configuration. The crystal field of tetragonal symmetry should split the ^{7}D$_5$ level into eight Stark components (^{7}D$_5 = \Gamma_1 + 2\Gamma_2 + \Gamma_3 + \Gamma_4 + 3\Gamma_5$). In order to find the relative energy position of the Stark components, it is necessary to construct the basic functions for the Γ_{1-5} irreducible representations, and then to calculate the matrix elements of the electrostatic potential on the Tb^{3+} ion, for each one of the eight Stark components. In this approximation the total angular momentum J, is the good quantum number (J–J coupling). However in order to avoid the lengthy calculations a different approach can be applied considering the orbital angular momentum of the d electron ($L = 2$) to be the good quantum number. In this first order approximation the Γ_4 irreducible representation, has the lowest energy in tetragonal site symmetry. The next irreducible representation with higher energy to the Γ_4 is the Γ_5 one, followed by the Γ_3 and the Γ_1. The Γ_2 and the Γ_5 Stark components are double and triple degenerate, and the degeneracy can be raised when the L–S coupling strength is strong enough within the levels of the 4f^{7}5d electronic configuration. The splitting of the levels of the 4f^{7}5d electronic configuration due to the L–S coupling is only few hundredth wave numbers, and this value is considerably smaller than the crystal field splitting. In the case of the LiLuF$_4$:Tb^{3+} ions, from the eight Stark components of the ^{7}D$_5$ level, of the 4f^{7}5d electronic configuration at 47.0×10^3 cm^{-1} (213 nm), 52.0×10^3 cm^{-1} (192 nm), 54.4×10^3 cm^{-1} (184 nm), 55.5×10^3 cm^{-1} (180 nm), 55.9×10^3 cm^{-1} (179 nm), 62.2×10^3 cm^{-1} (161 nm), 64.3×10^3 cm^{-1} (155 nm) and 67.5×10^3 cm^{-1} (148 nm) six are observed in the spectral range from to 155 to 200 nm, Fig. 1. We assign therefore the triple degenerate Γ_5 Stark component to the energy levels at 54.4×10^3, 55.5×10^3, and 55.9×10^3 cm^{-1}, and the double degenerate Γ_2 Stark component to the energy levels at 62.2×10^3 and 64.3×10^3 cm^{-1}, respectively, and the edge of the levels of the 4f^{7}5d electronic configuration in the LiLuF$_4$ host was found to be at 45.2×10^3 cm^{-1}.

The laser-induced fluorescence (LIF) spectrum in the spectral range from 153 to 200 nm, under excitation at 157.6 nm, with the F$_2$ laser, for 0.01 at.% concentration of the Tb^{3+} ion is shown in Fig. 2. The fluorescence peaks were assigned to the dipole allowed transitions between the levels of the 4f^{7}5d electronic configuration and the levels of the 4f^8 electronic configuration of the Tb^{3+} ion. This
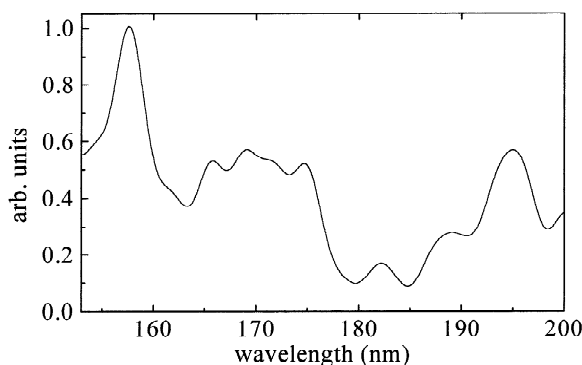

Fig. 2. Laser-induced fluorescence spectrum of the LiLuF$_4$:Tb^{3+} crystal. The concentration of the Tb^{3+} ion in the LiLuF$_4$ crystal was 0.01 at.%.

pumping arrangement has the advantage to populate the levels of the $4f^7 5d$ electronic configuration directly from the ground level of the Tb^{3+} ion, via one photon transition only. When the Tb^{3+} ion is excited from its $4f^8(^7F_6)$ ground level, to a given level of the $4f^7 5d$ electronic configuration, our experimental evidences indicate that it populates the levels of the $4f^8$ electronic configuration, when it is deexcited, from both the levels and the edge of the $4f^7 5d$ electronic configuration. The emission spectrum, which covers the spectral region from 193 to 220 nm, can be assigned to the dipole transitions between the Γ_5 Stark component of the $4f^7 5d(^7D_5)$ electronic configuration, with maximum of absorption at 54.4×10^3 cm^{-1} and the levels of the $4f^8$ electronic configuration. The Frank–Condon factor of the corresponding transitions, has its highest value at $52.9 \pm 0.2 \times 10^3$ cm^{-1}. The transition around 194 nm could originate as well from the Γ_3 Stark component with maximum of absorption at 51.6×10^3 cm^{-1}. The emission spectrum, which covers the spectral range from 159 to 174 nm, can be assigned to the dipole transitions between the Γ_2 Stark component of the $4f^7 5d(^7D_5)$ electronic configuration, and the levels of the $4f^8$ electronic configuration:

$$4f^7 5d\,[^7D_5(\Gamma_2),\, 62.6 \times 10^3 \text{ cm}^{-1}] \rightarrow 4f^8(^7F_6) + h\upsilon \text{ (159.7 nm)}$$

$$4f^7 5d\,[^7D_5(\Gamma_2),\, 62.6 \times 10^3 \text{ cm}^{-1}] \rightarrow 4f^8\,(^7F_4 \text{ or } ^7F_3) + h\upsilon \text{ (171 nm)}$$

$$4f^7 5d\,[^7D_5(\Gamma_2),\, 59.3 \times 10^3 \text{ cm}^{-1}] \rightarrow 4f^8\,(^7F_6) + h\upsilon \text{ (168.6 nm)}$$

$$4f^7 5d\,[^7D_5(\Gamma_2),\, 59.3 \times 10^3 \text{ cm}^{-1}] \rightarrow 4f^8\,(^7F_4) + h\upsilon \text{ (174.1 nm)}$$

Finally, the transitions at 166.1 and 174.8 nm, can be assigned to the interconfigurational transitions which are originating from the energy position at 60.2×10^3 cm^{-1}.

4. Conclusions

In conclusion, the LIF and the absorption spectra of the $LiLuF_4$:Tb^{3+} single crystals were studied in the VUV region of the spectrum. The LIF spectrum, in the spectral region from 150 to 200 nm, originate from the interconfigurational dipole transitions between the levels of the $4f^7 5d$ electronic configuration and the low levels of the $4f^8$ electronic configuration. These experimental results suggest that the $LiLuF_4$:Tb^{3+} crystal can be used as strong VUV photon energy converter from 157 nm, to wavelength between the 157 and 193 nm. The conversion efficiency depends strongly on the crystal purity. Because most of the photo resists which are potential candidates for VUV lithography have the right absorbance around 170 nm, the $LiLuF_4$:Tb^{3+} crystal can provide a new lithographic light source as a back-up solution to 157 nm photolithography.

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