Appl. Phys. A 74, 109–113 (2002) / Digital Object Identifier (DOI) 10.1007/s003390100975

Applied Physics A
Materials
Science & Processing

Rapid communication

Luminescence properties of thin films prepared by laser ablation of Nd-doped potassium gadolinium tungstate

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Received: 25 July 2001/Accepted: 26 July 2001/Published online: 17 October 2001 –

Abstract. Optically active thin films on Si substrates have been produced by laser ablation of a Nd-doped potassium gadolinium tungstate (Nd:KGW) single crystal. Films grown at low oxygen pressures (< 0.6 mbar) are potassium-deficient and appear to be mainly disordered. They show a poor photoluminescence (PL) performance that improves upon annealing in air at temperatures in the range 700–1000 °C. Films grown at high oxygen pressure (1 mbar) show instead good stoichiometry and the presence of a dominant textured gadolinium-tungstate phase compared to KGW. These films have low absorption, a refractive index close to that of bulk KGW and good PL performance, the emission lifetimes being longer ($\tau > 150\,\mu$s) under certain conditions than those measured in the single-crystal material.

PACS: 81.15.Fg; 42.70.Hj; 78.20.Ek

In the last few years, increasing attention has been paid to the preparation of passive and active waveguides that are of great interest as components for integrated optics and optoelectronics. Nevertheless, the development of devices in which generation, amplification, non-linear conversion, modulation, guiding and detection of light signals can be performed on one substrate is still a challenge. Among the possible material candidates for these applications, potassium gadolinium tungstate $KGd(WO_4)_2$ (KGW) doped with rare-earth ions (RE) such as Nd, Er or Yb is very promising [1–7], since Nd:KGW can be diode-pumped [6, 8–11], has a lower threshold and a higher slope efficiency (more than a factor of two) than Nd:YAG lasers [1, 3, 4, 12] and very efficient and ultra-low-threshold stimulated Raman scattering [9, 11]. These properties make this material interesting for a broad range of applications in communications, integrated optics, laser spectroscopy, ellipsometry, rangefinders and Raman spectroscopy.

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Pulsed laser deposition (PLD) has recently produced promising results in the synthesis of optical thin films and waveguides, as in the case of active materials doped with RE such as Er [13], Er–Yb [14], Eu [15] and Nd [16–18]. Doping with Nd has been performed either in YAG [16] or $Gd_3Ga_5O_{12}$ (GGG) [17] and very recently in KGW [18]. In that case, films grown on sapphire exhibited photoluminescence (PL) at 1.068 μm. Nevertheless, the growth of such active material on substrates compatible with Si technology would be highly desirable to build up integrated devices. Thus, the aim of the present work is to test the feasibility of the growth of Nd:KGW films with good luminescence properties on Si. The effects of the substrate temperature and the oxygen pressure during growth on the properties of the films have been studied in order to determine the conditions that lead to the optimum structural and luminescence properties.

1 Experimental

PLD films were grown from a KGW single-crystal target doped with 3 at. % of Nd (equivalent to 0.62 wt. % = 1.9×10^{20} Nd^{+3} ions cm^{-3}) using a KrF excimer laser (248 nm; 12 ns; repetition rate of 15 Hz) focused on the target surface at an angle of incidence of 45° to lead to a laser fluence close to 3 J cm^{-2}. Si (100) substrates were located at 30 mm in front of the target and the substrate temperature (T_s) was in the range 600–800 °C. The base pressure of the system was better than 2×10^{-5} mbar and the films were grown at different oxygen pressures in the range 0.1–1 mbar, for which the average deposition rate was in the range 0.7–0.5 nm s^{-1}. The thickness of the films was in all cases in the range 500–800 nm.

A He–Ne laser beam (633 nm) was used to record in real time the evolution of the reflectivity of the substrate as the films were growing. This allowed us both to control the synthesis process and to determine the film refractive index and the thickness by comparison with the reflectivity calculated for an isotropic planar two-layer (film and substrate) system [19]. The photoluminescence measurements were performed at room temperature using a monochromator

(resolution≈ 1.5 nm) and a liquid-nitrogen-cooled Ge detector, the latter being connected to a lock-in amplifier or to a digital oscilloscope for PL intensity and lifetime measurements respectively. An Ar^+ laser tuned at the 0.514-μm line was used as the excitation source (output power 140 mW). The beam was incident at 25° with respect to the sample normal and the PL signal was collected along the perpendicular to the film plane. In order to determine if the PL features could be further improved [14, 18], post-deposition thermal anneals were performed by heating the films in air for 1 h at increasing temperatures in the range 600–1100 °C in 100 °C steps. The PL features were measured after each annealing step at room temperature and the films were subsequently annealed to the next temperature.

The composition of the films was analyzed by means of Rutherford backscattering spectrometry (RBS) using a 1.8-MeV He^+ beam and a scattering angle of 165°. The elemental composition was calculated through the simulation of the measured spectra by means of the RUMP computer code [20]. The Nd content could not be accurately determined, due to the proximity of its signal to that of Gd. X-ray diffraction (XRD) with Cu K_α radiation was used in the θ–2θ Bragg–Brentano geometry to determine the crystallographic structure of the films.

2 Results

Figure 1 shows both the real (n) and the imaginary (k) parts of the refractive index of the films grown at a substrate temperature of 650±20 °C as a function of the oxygen pressure applied during deposition. It is seen that the values of n remain nearly constant and close to 1.95, this value being very similar but on the lower limit to that of Nd:KGW single crystal [2, 8]: $n = 1.95$ (for an axis parallel to the (010) axis), $n = 2.00$ (for an axis at 24° with respect to the (100) axis) and $n = 2.05$ (for an axis at 20° with respect to the (001) axis). The values of k are low in all cases, although they slightly increase up to 0.07 with the oxygen pressure. The experimental values obtained for films grown at substrate temperatures below 720 °C for the same oxygen-pressure interval (not shown here) are similar ($n = 1.9$±0.1 and $k < 0.08$); nevertheless, a dramatic decrease of n (< 1.7) and an increase of k (> 0.15) are observed for temperatures above 760 °C. Thus the results presented from now on correspond to films grown at a substrate temperature of 650±20 °C.

The analysis of the RBS measurements shows that the ratios of the numbers of O atoms (N_O) and Gd atoms (N_{Gd}) to the number of W atoms (N_W) are $N_O/N_W = 4.2$±0.4 and $N_{Gd}/N_W = 0.55$±0.05 for oxygen pressures in the range 0.1–1.0 mbar and thus they are close to the stoichiometric values (4 and 0.5, respectively). The errors given correspond to the dispersion of the data for the different films grown under similar experimental conditions or to the experimental error in the determination of the atomic content by RBS, whichever is greater. The ratio of the number of K atoms (N_K) to N_W depends instead on the oxygen pressure as shown in Fig. 2. The films are K-deficient for low oxygen pressures and they become stoichiometric for oxygen pressures ≥ 0.6 mbar. Films grown at 0.1 mbar will be from now on referred to as K-deficient films.

XRD scans of films grown at 0.1 mbar (a) and 1 mbar (b) of oxygen pressure are shown in Fig. 3. The XRD scan of the film grown at 0.1 mbar shows a sharp but modest peak at 9.7° and a very weak and broad band between 28.3° and 30°. When the oxygen pressure is increased, new diffraction peaks appear. Films grown at 1 mbar (Fig. 3b) show a much more intense and dominant peak at 9.7° and minor peaks at 17.0°, 19.6°, 22.0°, 29.4°, 34.3°, 39.7°, 44.9° and 50.2°. According to the available data [21], the peak at 9.7° cannot be attributed to any KGW line but instead to monoclinic gadolinium tungstate Gd_2WO_6 (GW). Half of the observed minor peaks can thus be related to higher orders of diffraction ($n = 2$ to 5) of the main peak at 9.7°, the others at 17.0°, 22.0°, 34.3° and 44.9° being respectively attributed to the (020), (040), (200) and (400) lines of KGW. These results suggest that nearly disordered films are produced at 0.1 mbar of oxygen pressure while polycrystalline films containing KGW and GW are produced at 1 mbar.

Figure 4 shows the PL spectra of the as-grown films at 0.1 mbar (a) and 1 mbar (c) of oxygen pressure. It is clearly seen that the films exhibit two spectral bands peaking at 1.06 μm and 1.35 μm. These bands are broad and nearly featureless for films grown at 0.1 mbar of oxygen pressure (Fig. 4a), whereas they show several features in films grown at 1 mbar of oxygen pressure (Fig. 4c) that recall the resolved peaks due to the Stark sub-levels that appear in the single-crystal material (Fig. 4e). This last spectrum was col-

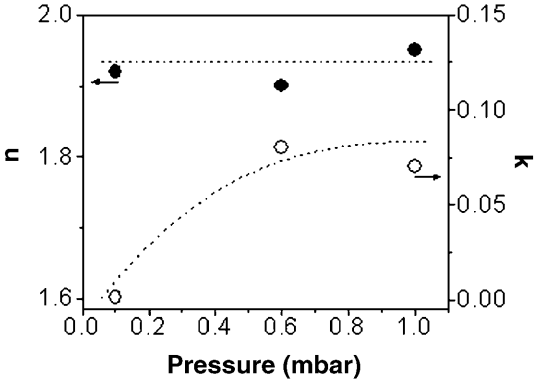

Fig. 1. Real n(●) and imaginary k(○) parts of the refractive index of films deposited at $T_s = 650 \pm 20$ °C as a function of the oxygen pressure. The *dashed lines* are a guide for the eye

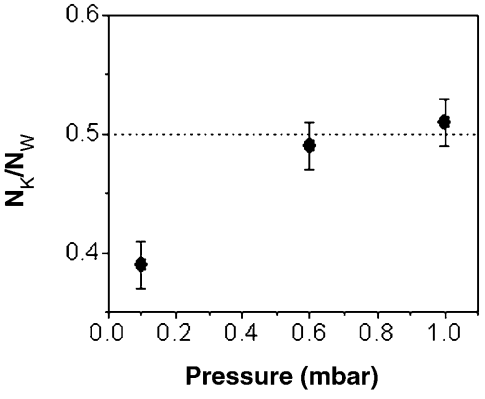

Fig. 2. Ratio of numbers of K atoms to W atoms (N_K/N_W) of films deposited at T_s =650±20 °C as a function of the oxygen pressure. The *dashed line* corresponds to the stoichiometric N_K/N_W ratio

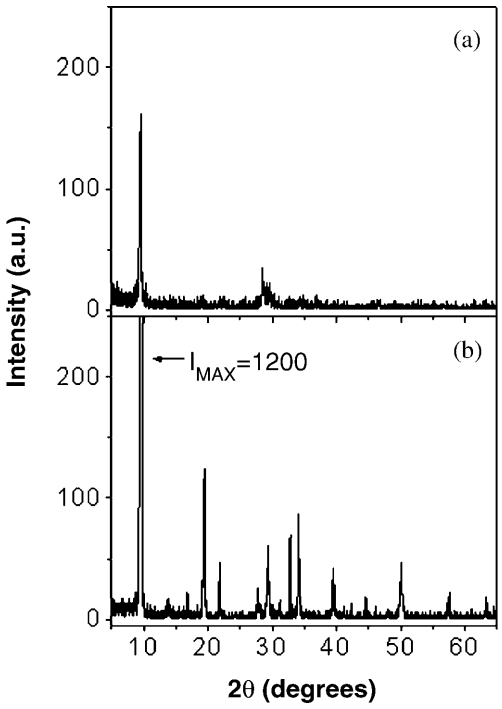

Fig. 3. XRD scan of films deposited at T_s =650±20 °C and at oxygen pressures of (a) 0.1 mbar and (b) 1 mbar

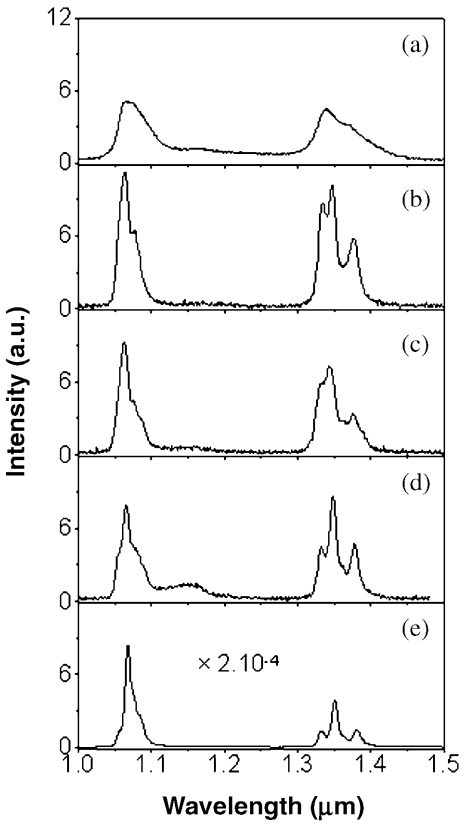

Fig. 4. PL spectra of films grown at T_s =650±20 °C and at oxygen pressures of (a), (b) 0.1 mbar and (c), (d) 1 mbar. The spectra (a), (c) correspond to the as-grown films and (b), (d) to the films step-annealed up to 800 °C. The PL spectrum recorded from the target (e) is included for comparison. The spectrum in (e) is multiplied by a factor of 2×10^{-4} in order to ease the comparison

lected from the target under the same conditions as those of the films, although its intensity has been multiplied by a factor of 2×10^{-4} to ease the comparison. Similar spectra were also collected from a lasing crystal of KGW excited along the (100), (010) or (001) axis, respectively. Although some differences were seen when changing the excitation direction, the overall shape of the spectra is always similar to that shown in Fig. 4e. In this sense, it is worth pointing out that whereas the ratio of emission intensity of the 1.06-μm band to that of the 1.35-μm band is close to two for the single crystal, this ratio is near to one in the case of the thin films. Annealing of samples in air above 700 °C induces changes in the shape of the PL spectra. Resolved peaks for both emission bands appear in the film grown at 0.1 mbar (Fig. 4b) and the shape of each band approaches that of the single-crystalline material in the films grown at 1 mbar (Fig. 4b and d).

The PL lifetime corresponding to the 1.06-μm band measured in films grown at 0.1, 0.6 and 1 mbar of oxygen pressure is included in Fig. 5 as a function of the annealing temperature. The lifetime values for the 1.35-μm band are equal within experimental errors to those for the 1.06-μm one, as expected from the fact that both arise from the same initial excited level. The lifetime increases as the oxygen pressure increases in the case of the as-grown films, the longest lifetime value being 160 μs for films grown at 1 mbar. Upon annealing the films, the PL lifetime measured in films grown at 0.1 mbar of oxygen pressure increases significantly, whereas that of films grown at 1 mbar follows the opposite trend. Films grown at an intermediate oxygen pressure, namely 0.6 mbar, show a nearly temperature-independent lifetime value close to 120 μs, this value being the one at which the PL lifetimes measured for films grown at 0.1 mbar and 1 mbar tend upon annealing.

3 Discussion

The results presented here clearly show that the oxygen pressure is a critical parameter controlling the composition and the crystalline quality of the films. Although the growth of polycrystalline Nd:KGW films on sapphire by PLD at 0.1 mbar of oxygen pressure has been reported earlier [18], the present results clearly show that a higher pressure (1 mbar) is required in the case of Si substrates to achieve the KGW stoichiometry. The reasons for these differences are most likely related to the better lattice matching between KGW and sapphire, similarly to what has earlier been reported for $LiNbO_3$ [22, 23].

The XRD analysis shows that films grown at the most favorable pressure (1 mbar) contain an appreciable quantity of GW. Furthermore, this phase is most likely textured since there is only one dominant peak (at 9.7°) observed in all cases. To account for the KGW global stoichiometry revealed by RBS and shown in Fig. 2, there must thus exist also a phase containing an excess of potassium, although no evidence for it is seen in the XRD scan. The XRD procedure used in this work only allows us to see the crystalline material textured parallel to the plane of the substrate. Therefore, this potassium-rich phase is either amorphous or crystalline and oriented in a direction out of the plane of the substrate. Similarly, the appearance of only weak peaks related to KGW suggests that the samples do not contain much

of such phase textured in the plane of the substrate. It is worth pointing out that in an earlier work related to the production of KGW films on sapphire by PLD [18], the XRD analysis started at 15° and thus the strong reflection of GW at 9.7° – if it existed – could not be seen. Nevertheless, the absence or minimal height of the higher-order reflections at 19.5°, 29.5° and 39.6° of GW suggests that the quantity of textured GW in that earlier work, if any, should have been small.

The refractive index of the films is similar to that of bulk single-crystal KGW although the films appear to be slightly more absorbing. As the oxygen pressure is decreased, i.e. the films become K-deficient, only slight variations are observed in the optical properties and these relate mainly to a decrease of the film absorption (see Fig. 1). K-deficiencies have nevertheless dramatic consequences in the PL performances as seen in Figs. 4 and 5. It is well known that although the energy levels of the RE-related optical transitions are little affected by the environment, the shape of the emission spectrum is strongly affected. It is normally featureless for amorphous or disordered hosts, as opposed to the resolved emission peaks related to the Stark sub-levels for ordered environments in crystalline hosts (such as in the case of the target in Fig. 4e). Our results show that the use of low oxygen pressures leads to K-deficient films, which exhibit a nearly featureless spectrum, which supports further the conclusion that these films are amorphous. The change in the PL spectrum after annealing above 700 °C (Fig. 4b) indicates that this treatment leads to a more-ordered structure. The shape of the PL spectrum of the films grown at 1 mbar is instead consistent with an ordered host (Fig. 4c, d) and no significant changes are observed upon annealing.

The PL lifetime obtained for the as-grown films is high and increases as the oxygen pressure increased. For the film grown at 1 mbar of oxygen pressure, it is even longer (160 μs) than that measured under the same conditions for the bulk material along different crystalline axes: 134 μs for (100), 149 μs for (010) and 152 μs for (001). The higher lifetime might be related to the different environment of Nd ions due to the presence of GW. It is worth pointing out that the lifetime measurements included in Fig. 5 are the first reported lifetime values in films grown by laser ablation of Nd:KGW, and thus no comparison of the PL performances to the earlier reported results of films grown on sapphire is possible [18]. In that earlier work, the quality of the films was evaluated through the measurement of the full width at half maximum (FWHM) of the emission at 1.06 μm, the value being 6.5±2.1 nm. The results observed in the present work show that the FWHM corresponding to the 1.06-μm emission are 13 nm, 18 nm and 50 nm for the target, the optimum films grown at 1 mbar and the K-deficient films respectively. Whether the broader FWHM measured in this work is related to a higher disorder in the films grown on Si, to the presence of the GW phase or to the different excitation conditions is not clear at this point.

The comparison of the lifetime values for the films grown at 1 mbar and 0.1 mbar of oxygen pressure shows that the latter has a much shorter lifetime (< 25 μs) than the former. The small variations of the lifetime upon annealing observed in the case of films grown at 1 mbar compared to the large variation in the latter case supports further the idea that the K-deficient films are initially amorphous and become ordered upon annealing, as the spectra in Fig. 4 suggest. The sharp increase of the lifetime in the K-deficient films is thus most likely related to the crystallization of the films.

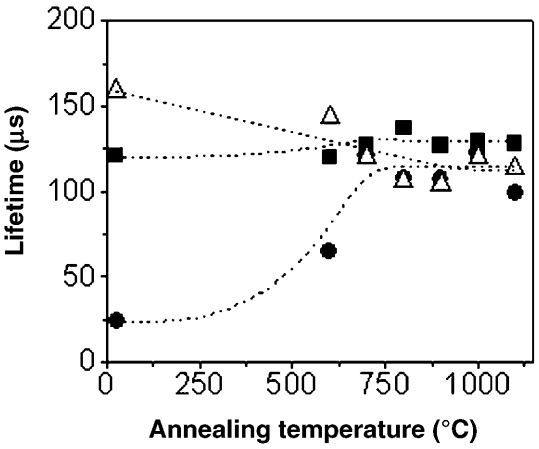

Fig. 5. PL lifetime at 1.06 μm of films grown at $T_s = 650 \pm 20$ °C and at oxygen pressures of (●) 0.1 mbar, (■) 0.6 mbar and (△) 1 mbar. The *dashed lines* are a guide for the eye

4 Conclusions

Nd-doped films with good crystallinity and photoluminescence response have successfully been grown on Si by pulsed laser ablation of Nd:KGW under optimized growth conditions: a substrate temperature of 650–700 °C and an oxygen pressure of 1 mbar. The lifetime value for the emission at 1.06 μm (160 μs) is even longer than that measured in the single-crystal material, this result being most probably related to the formation of GW. At lower oxygen pressures, films were found to be K-deficient and mainly disordered. Their poor PL performances improve upon annealing in air up to 700 °C, this improvement being consistent with the crystallization of the films.

Acknowledgements. P.A.A. and J.A.C. acknowledge respectively the Scientific Committee of NATO and the Spanish Ministry of Educación y Cultura for financial support. We thank Dr.A. Cebollada from the Instituto de Microelectrónica de Madrid (CSIC) for assistance with the XRD analysis and helpful discussions. This research was partially supported by CYCIT (Spain) under Project No. TIC1999-0866. We acknowledge the assistance of the Spanish–Bulgarian Bilateral Agreement for traveling support.

References

1. V. Kushawaha, A. Banerjee, L. Major: Appl. Phys. B **56**, 239 (1993)
2. I.V. Mochalov: Opt. Eng. **36**, 1660 (1995)
3. R. Moncorgé, B. Chambon, J.Y. Rivoire, N. Garnier, E. Descroix, P. Laporte, H. Guillet, S. Roy, J. Mareschal, D. Pelenc, J. Doury, P. Farge: Opt. Mater. **8**, 109 (1997)
4. O. Musset, J.P. Boquillon: Appl. Phys. B **64**, 503 (1997)
5. N.V. Kuleshov, A.A. Lagatsky, V.G. Shcherbitsky, V.P. Mikhailov, E. Heumann, T. Jensen, A. Diening, G. Huber: Appl. Phys. B **64**, 409 (1997)
6. A.A. Lagatsky, N.V. Kuleshov, V.P. Mikhailov: Opt. Commun. **165**, 71 (1999)
7. M.C. Pujol, M. Rico, C. Zaldo, R. Solé, V. Nikolov, X. Solans, M. Aguiló, F. Díaz: Appl. Phys. B **68**, 187 (1999)
8. T. Graf, J.E. Balmer: Opt. Eng. **34**, 2349 (1995)

9. V. Kushawaha, Y. Yan, Y. Chen: Appl. Phys. B **62**, 533 (1996)
10. P. Karlitchek, G. Hillrichs: Appl. Phys. B **64**, 21 (1997)
11. A.A. Demidovich, A.N. Kuzmin, G.I. Ryabtsev, W. Strek, A.N. Titov: Spectrochim. Acta A **54**, 1711 (1998)
12. A.A. Demidovich, A.P. Shkadarevich, M.B. Danailov, P. Apai, T. Gasmi, V.P. Gribkovskii, A.N. Kuzmin, G.I. Ryabtsev, W. Strek, A.N. Titov: Appl. Phys. B **67**, 11 (1998)
13. R. Serna, C.N. Afonso: Appl. Phys. Lett. **69**, 1541 (1996)
14. R. Serna, J.M. Ballesteros, M. Jimenez de Castro, J. Solis, C.N. Afonso: J. Appl. Phys. **84**, 2352 (1998)
15. S.L. Jones, D. Kumar, R.K. Singh, P.H. Holloway: Appl. Phys. Lett. **71**, 404 (1997)
16. M. Ezaki, H. Kumagai, K. Kobayashi, K. Toyoda, M. Obara: Jpn. J. Appl. Phys. Part 1 **34**, 6838 (1995)
17. D.S. Gill, A.A. Anderson, R.W. Eason, T.J. Warburton, D.P. Shepherd: Appl. Phys. Lett. **69**, 10 (1996)
18. P.A. Atanasov, R.I. Tomov, J. Perrière, R.W. Eason, N. Vainos, A. Klini, A. Zherikhin, E. Millon: Appl. Phys. Lett. **76**, 2490 (2000)
19. M. Born, E. Wolf (eds.): *Principles of Optics* (Pergamon, New York 1980) p. 51
20. L.R. Doolittle: Nucl. Instrum. Methods B **9**, 344 (1985)
21. EPSRC's Chemical Database Service, Daresbury Laboratory, UK (2000); D.A. Fletcher, R.F. McMeeking, D.J. Parkin: J. Chem. Inf. Comput. Sci. **36**, 746 (1996)
22. J.A. Chaos, V. Puneri, J. Gonzalo, C.N. Afonso: J. Appl. Phys. **88**, 3768 (2000)
23. J.A. Chaos, J. Gonzalo, C.N. Afonso, J. Perriere, M.T. García-González: Appl. Phys. A **72**, 705 (2001)