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Laser-produced plasma ion characteristics in laser ablation of lithium manganate

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Abstract

Laser ablation is widely used to assist in the fabrication of prototype lithium manganate ($LiMn_2O_4$) thin film structures for Li-ion battery electrodes via the pulsed laser deposition technique. However, films can be considerably Li and/or O deficient, depending the deposition conditions used. Here we present data on the ionic component of laser-produced plasma in laser ablation of lithium manganate with ns excimer laser. Plasma was monitored using an electrical Langmuir ion probe, in time-of-flight mode in conjunction with mass spectrometry to identify the dominant ionic species. Ablation in vacuum at $\sim$2.5 J cm^{-2} revealed the plasma's ionic component was composed primarily of singly charged Li and Mn ions. The time-of-flight data indicates significant deceleration of the plasma when ablation is carried out in an oxygen background gas pressure of the order of 10 Pa. The implications for thin film growth are considered in terms of the possible gas phase interactions and/or thin film re-sputtering yield.
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1. Introduction

There has been considerable interest in the development of prototype thin film Li-oxide structures and devices for the purpose of characterising novel Li-ion battery cathode composites and also for thin film battery (e.g. micro-battery) fabrication [1]. Recent developments indicate that hybrid composites, benefiting from the superior cycling stability of lithium cobalt oxide (LCO) and the safer overcharge tolerance of lithium manganese oxide (LMO), could emerge as the replacement technology for conventional LCO-based Li-ion battery cathodes [2]. Pulsed laser deposition (PLD), which essentially involves the transfer of a target material to a suitable substrate via laser ablation, is widely used to prepare novel thin film compositions and structures [3]. In PLD of Li-containing oxides, Li and O composition is strongly affected by several factors: the substrate temperature [4], background gas

(usually O_2) pressure [5] and target-substrate separation. These compositional deficiencies can be overcome, e.g. by use of a Li-rich target [6,7] or by optimising background gas pressure and type [8], but there is scope for a more rigorous understanding of the underlying mechanisms involved, particularly as the above-mentioned need for scanning a wider compositional parameter space arises. The effect of substrate temperature appears to be adequately described by Li out-diffusion [4] and oxidation kinetics [9], with films grown at substrate temperatures above 600 °C typically Li and/or O deficient. While the role of oxygen pressure is not exactly clear, films grown in high vacuum or low (<1 Pa) O_2 background gas pressures are also Li and O deficient (typically 10% deficiency) and the Li deficiency appears to be increased at larger target-substrate distances in O_2 [7]. Such pressure-distance dependency generally indicates that the dynamics of the laser-produced plasma and its interaction with the background gas play an important role in the PLD environment. Plasma diagnostics are extremely useful in this regard, providing temporal and/or spatial resolution of parameters such as concentration of various neutral or ionic species and their corresponding energy distributions. However,

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whilst there are several comprehensive plasma diagnostic studies (see, for example [10], and references therein) reported on similar deficiency behaviour in other Li-oxide systems such as LiNbO$_3$, there appears to be very little reported [11,12] on the LMO system.

In this paper, we report on a preliminary investigation of the ionic component of the laser-produced plasma in PLD of LMO using an electrical ion probe and mass spectrometry. The aim of this study was to quantify some of the primary ionic characteristics of the laser-produced plasma, e.g. ion flux and ion energy, and to establish whether there is any correlation between the measured ionic behaviour and LMO thin film deficiencies.

2. Experimental setup

The experimental setup [13] for this study was based on a turbo-pumped chamber capable of attaining ultimate vacuum of $\sim 10^{-4}$ Pa and a KrF excimer ($\tau = 25$ ns, $\lambda = 248$ nm) laser operated at 10 Hz repetition rate, with laser fluence varied by means of a variable transmission window. The cylindrical ceramic target was prepared from LiMn$_2$O$_4$ powder (Honeywell, Specialty Chemicals, 99.7% purity), pressed at 0.2 GPa and sintered for 24 h at 750 °C. The beam was focused by a single lens yielding a spot-size of 2 mm × 1 mm on the target and ablation was carried out in high vacuum or a "static" O$_2$ background gas at pressures ranging from high vacuum (10^{-4} to 30 Pa). The electrical (Langmuir) ion probe [14] consisted of a planar copper collector with a 1mm diameter circular cross-section operated in ion saturation mode ($V_{bias} = -30$ V) in order to repel electrons and collect a positive ion current [15]. The plane of the probe collector was aligned perpendicular to the target normal and translation of the probe along the target normal facilitated 1D spatial resolution up to a distance in the range 2–6 cm from the target at 5 mm intervals. Plasma was analysed separately by a Hiden Analytical quadrupole mass spectrometer (QMS) operated in positive ion collection mode, with the orifice position limited to a minimum distance of 10 cm from the target surface (along the target normal). Although the QMS acquisition sampling gate was limited to a minimum setting of 100 μs, this should provide adequate time to sample the majority of the plume's ionic species, considering the average expansion velocity of the plasma in vacuum is of the order of 1 cm/μs (see Fig. 5).

3. Results and discussion

3.1. High vacuum analysis

A typical positive ionic mass spectrum acquired using the QMS is presented in Fig. 1. Singly charged Li and Mn ions dominate the spectra and the two identified isotopes of Li (Li$_6$ and Li$_7$) have a count ratio that is close to the reported relative abundance (Li$_7$/Li$_6$ ~ 10) [16]. Significant signal was also detected at values of 23, 39 and 87 amu, which we have assigned to the ionic oxides LiO$^+$, LiO$_2^+$, and MnO$_2^+$, respectively. The origin of the signal at $M = 40$ amu has yet
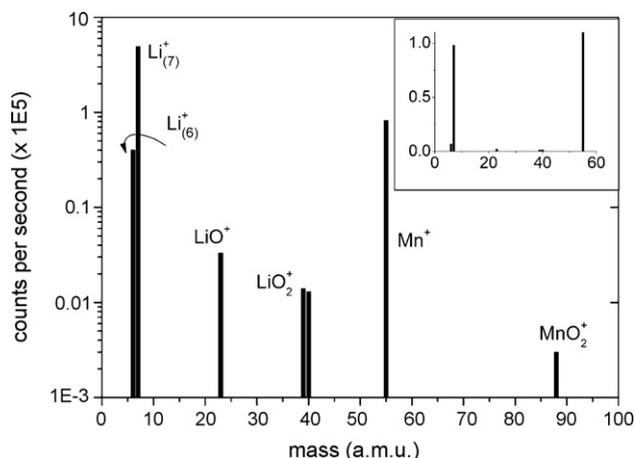

Fig. 1. QMS ionic mass spectra for laser ablation of LMO at 2.5 J cm^{-2} in high vacuum. The spectra is also corrected for a detector efficiency assuming an inverse mass dependency (inset), and normalized to the Li ($m = 7$ amu) count. The species at $m = 40$ amu may be a Ca impurity in the target. Spectra were acquired at 10 cm from the target. No signal was detected at masses above 100 amu.

to be established, though this could be due to a Ca$^+$ impurity (e.g. calcium carbonate) in the target due to powder impurity or sintering. This data is qualitatively similar to that reported by Zhou et al. [11,12], except for the absence of MnO ions in our spectra. Caution must be exercised when invoking the relative Li$^+$ and Mn$^+$ concentrations, since the transmission function for the QMS system was not calibrated for these species. As a first approximation however, the detector efficiency might be expected to scale inversely with ionic mass (i.e. $M_{Li}/M_{Mn} \sim 1/8$) [17], indicating that the concentrations of Li and Mn ions in the plasma is of the same order of magnitude (see Fig. 1, inset).

Ion time-of-flight (TOF) profiles, measured using the Langmuir probe in high vacuum at various laser fluence, are plotted in Fig. 2a. These profiles show a single broad TOF characteristic of a laser-produced plasma free expansion in vacuum [18]. The reduction of the "peak" TOF, i.e. corresponding to the time-of-arrival of the maximum ion flux to the probe, to shorter times is clearly evident as the fluence is increased. Corresponding energy distributions, $N(E)$, for the free expansion in vacuum were determined using the differential relation: $dN(E)/dE = (dN(v)/dv)(dv(E)/dE)$ where the current (I) collected by the probe is related to the collector area (A), the charge density (N_i) and ionic charge (eZ_i) by: $I = N_i eZ_i v$ (Fig. 2b). In the absence of mass-resolved TOF data, we cannot discriminate between various ionic species in the TOF spectra; therefore, the distributions were calculated using the mass of both dominant ionic masses (i.e. Li$_7$ or Mn) and an ionization degree of +1. At a fluence of 2.5 J cm^{-2}, typically used in PLD of lithium manganate, the distribution calculated using the higher mass value (i.e. $m_{Mn} = 55$ amu) extends to several hundred eV, with that of Li maximised near 100 eV.

The ion dose per second, $F_{ion} = f_{rep}/A_p \int I_P \, dt$, was determined from the integral of the ion probe current (I_P), the probe collector area (A_p) and the laser pulse repetition rate (f_{rep}) is plotted in Fig. 3. For comparison, the thin film growth
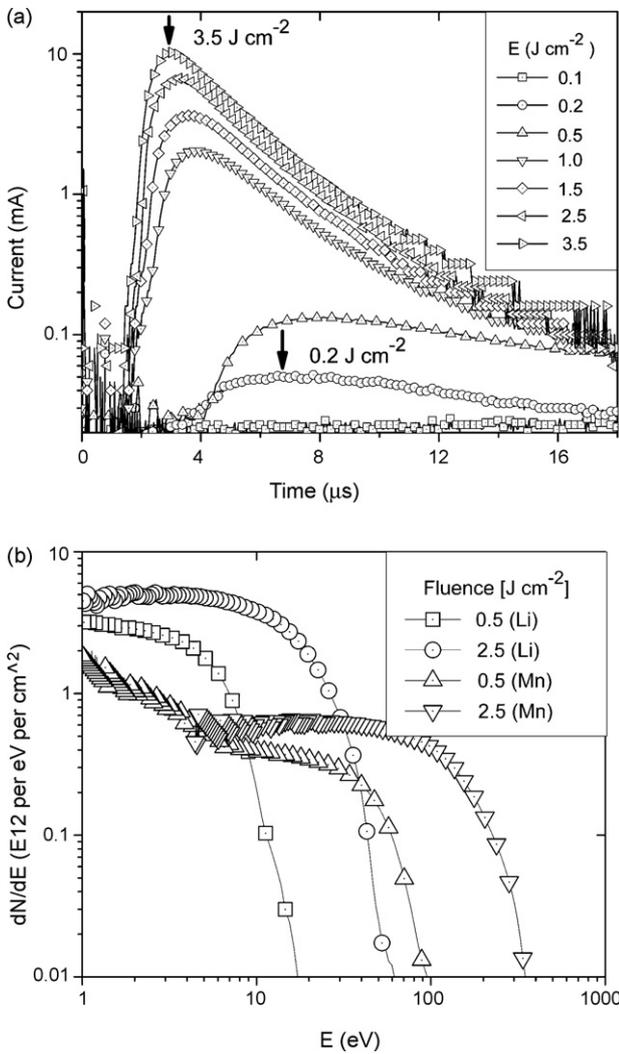
Fig. 2. Ion TOF data for LMO ablation at various fluence (a, top) and ion energy spectra (b, bottom) calculated using the TOF spectra at two fluence and either the mass of Li (7 amu) or Mn (55 amu).
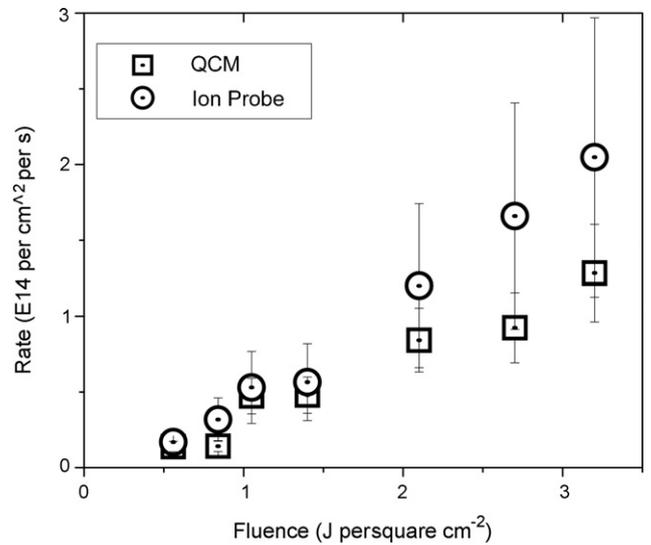

Fig. 3. Comparison of ion flux (circles) and growth rate (squares) as determined by the Langmuir probe and the quartz crystal monitor (QCM). The error bars correspond to the accuracy associated with measuring the Langmuir probe collector area and the fit to the QCM deposition rate (ng/(cm^2 s)) data, respectively. The error in laser fluence reading (not shown), including pulse-to-pulse energy fluctuations, was approximately 20%.

peaks, are plotted in Fig. 5. These profiles show the characteristic constant velocity ($\sim$1.9 cm/μs) of a vacuum-like expansion and the deceleration associated with plume expansion in a background gas [20]. At distances of 40 mm or more from the target, it is clear from Fig. 5 that the majority of the ions have been slowed significantly, from the vacuum velocity of 1.9 cm/μs to an instantaneous value of $\sim$0.1 cm/μs. Thus, we can expect that the directed kinetic energy of the ions to have reduced by a factor of about 100. It is noteworthy that our observations are qualitatively similar behaviour has been observed in PLD of lithium barium manganate ($La_{0.67}Ba_{0.33}MnO_3$) where the ion dynamics were correlated to the structural quality of the films [12].

rate of lithium manganate molecules in per unit area (cm^2) per second (F_{film}) as determined by a quartz crystal monitor (QCM) is also plotted in this figure, using the relation: $F_{film} = (\Delta m_{film}/M_{film})N_{Av}$. where Δm_{film} is the measured mass growth rate as determined by the QCM (g cm^{-2} s^{-1}) and N_{Av} is Avogadro's constant. These growth rate measurements were carried out on unheated substrates (i.e. at room temperature) and we have assumed that the molecular mass of the film, M_{film}, is equal to the stoichiometric value of 181 g mol^{-1}. This may underestimate the growth rate somewhat since the film stoichiometry for growth in vacuum is offset by the deficiency in Li and/or O.

3.2. Oxygen background analysis

The ion-probe TOF spectra for ablation in 10 Pa O_2 are plotted in Fig. 4. The general trend observed, i.e. a double-peak TOF, arises from collisions between the laser-produced plasma ions and the gas molecules and has been discussed extensively in the literature [19]. The distance-TOF profiles extracted from these measurements, noting the TOF of the first and second
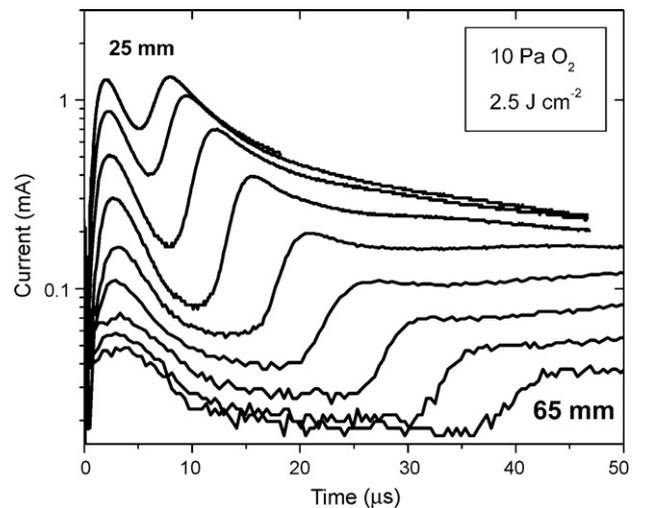

Fig. 4. Ion TOF profiles, measured at various distances from the target surface, for LMO ablation in 10 Pa O_2. The TOF values for the first (in vacuum) and second (delayed) peaks were extracted and used to determine velocity values (Fig. 5).
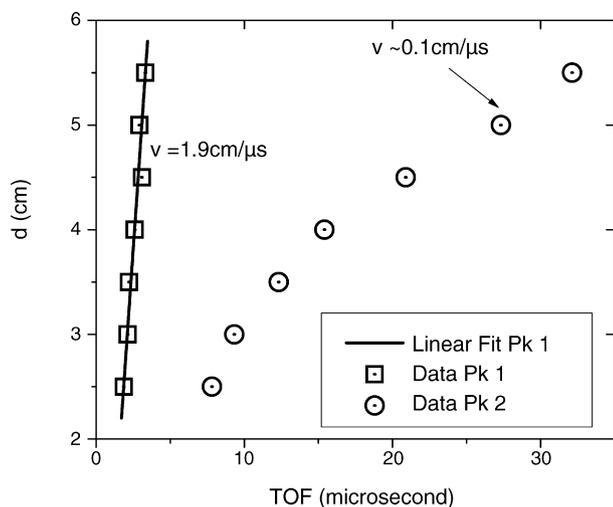
Fig. 5. Distance-TOF profiles for the in vacuum and background gas (10 Pa) expansions. The velocity of the vacuum expansion was determined from the slope of the straight-line data while the approximate velocity for the background gas data was calculated noting the instantaneous value from 50 to 55 mm.

Table 1
Thermodynamic and electronic properties of various components of the Li–Mn–O system

Species	M_r (g/mol)	E_c (kJ/mol)	$-E_i$ (eV)	$-\Delta H$ (kJ/mol)	$-\Delta G$ (kJ/mol)
Li	7	–	5.39	159	126.6
Mn	55	–	7.43	–	
O	16	–	13.6	–	–
Li2	14	–	5.1	–	174.4
LiO	23	–	8.45	–	333
LiO_2	39	878	–	–	–
Li_2O_2	46	2,592	–	−634	–
Li_2O	30	2,799	–	−598	−561.2
MnO	71	3,724	–	−385	−362.9
MnO_2	87	12,970	–	−520	−456.1
Mn_2O_3	158	15,146	–	−959	−881.1
Mn_3O_4	229			−1387	−1283.2
$LiMn_2O_4$*	181				−1570
$LiMnO_2$*					−950

E_c: lattice cohesive energy; E_i: first ionization potential; ΔH: heat of formation; ΔG: Gibbs free energy change. The ΔG values for the oxides are for oxidation of Li, Mn with molecular oxygen. From [24] except for *[25].

3.3. Implications for $LiMn_2O_4$ thin film growth

The main results of this preliminary study on the ionic characteristic of the laser-produced plasma in laser ablation of LMO can be summarised as follows: (i) the plume is primarily comprised of Mn and Li ions; (ii) calculated ion energy distributions extend to 100 eV and beyond; (iii) increasing the background gas pressure to about 10 Pa leads to considerable slowing of the laser-produced plasma ions. Let us firstly consider the ion characteristics in vacuum. It has been shown that film re-sputtering typically becomes significant when the average ion energies exceed a few tens of eV [21] for a wide range of materials. The approximation for the ion beam-sputtering yield (Y_F) given by Zalm [22] has been widely used to describe resputtering in PLD of multi-component metallic thin films [23]:

$$Y_F(E_p) = \frac{1.9}{U_0}\left(\frac{Z_F}{f}\right)^{1/2}\left(\sqrt{E_p} - 0.09\sqrt{U_0}\right)$$

This expression is primarily dependent on the cohesive energy (U_0) of the film species and the projectile (ion) energy E_p, measured in keV, and to a lesser extent on the target mass Z_F and a function (f) related to the ratio of the masses of the target and projectile species. While a correlation between film resputtering and a deficiency of lighter metals has previously been observed in PLD of transition-metal doped ZnO [24] using Zalm's approximation, there appears to be little in the way of specific data on the cohesive (bond) energies in the $LiMn_2O_4$ system and so it is difficult to quantify the yield in this case. Nevertheless, an overview of the available thermodynamic data [25,26] for various Li–Mn–O compounds indicates that, in general, Mn oxides have higher lattice energies and lower Gibbs free energies than Li oxides (Table 1). This would suggest that the Mn–O bond should be more stable than any Li–O bond in the $LiMn_2O_4$ structure. It also may also be worth

considering the approach taken by Malherbe et al. [27] in determining the bond energy and corresponding resputtering yield for a wide range of oxide compounds. Their calculations show remarkably good agreement between theory and experiment and suggest a strong correlation between the metal and oxygen ratio in the sputtered films and the mass of the metal species in the oxide, with lighter metals being more easily sputtered. Nevertheless, as highlighted previously [3,22], the quantitative accuracy of these models may need to be reconsidered when relatively light projectile (i.e. Li) species are involved. Re-sputtering is unlikely to be significant at O_2 pressures of the order of 10 Pa, since ion energies of the order of several tens of eV are usually required to achieve significant sputtering yield [22]. In fact, it has been noted previously that the growth rate of lithium manganate thin films as a function of oxygen pressure, measured using a quartz crystal monitor, is maximised when using an O_2 pressure of 20 Pa [28]. Indeed it seems that it is worth carrying out more quantitative analysis of the possibility of resputtering in PLD of lithium manganate, considering our observations and the fact that many studies report that the Li and/or O deficiencies observed when PLD is carried out in high vacuum can be corrected by use of an oxygen background pressure of about 10 Pa.

In addition to suppressing the re-sputtering potential of the laser-produced plasma, the O_2 background may affect the lithium manganate growth process by preferentially scattering lighter species, i.e. Li, as observed in PLD of lithium niobate [29]. The possibility of gas-phase reactions must also be considered since laser ablated Li and LiO_2 are known to react with molecular oxygen forming oxides such as LiO_2 or LiO_2Li [30]. We have not observed a delayed release of Li as reported in PLD of LNO [31], though the neutral component of the laser-produced plasma would have to be analysed to confirm this. Ultimately, a more detailed analysis of the laser-produced plasma, including for example angular resolved studies of the individual species dynamics, is required to confirm these aspects.

4. Conclusion

To summarise, the ion dynamics of the laser-produced plasma in laser ablation of a ceramic $LiMn_2O_4$ target were monitored using an electrical Langmuir probe. Using mass spectrometry, the plasma's ionic component was shown to be comprised primarily of singly charged Li and Mn ions, when ablation is carried out at fluence of a few Joules per square cm. Time-of-flight profiles show that, compared with ablation in high vacuum, the characteristic expansion velocity of the plasma is greatly reduced by the introduction of O_2 to a pressure of the order of 10 Pa, which is typically used in PLD of lithium manganate. The time-of-flight spectra also indicate that the average ion energy of Mn ions may extend to several hundred eV, suggesting that film resputtering should be significant in PLD of lithium manganate when carried out in high vacuum. This has been related to the widely reported deficiencies of lithium and oxygen in PLD of lithium manganate, though a quantitative analysis of preferential resputtering requires more detailed information on the cohesive energies of the film constituents and a review of the existing sputtering models applicable to PLD of such materials.

Acknowledgements

References

[1] M.M. Thackeray, C.S. Johnson, J.T. Vaughey, N. Li, S.A. Hackney, J. Mater. Chem. 15 (2005) 2257–2267.

[2] B. Ammundsen, J. Paulsen, Adv. Mater. 13 (2001), 943-+.

[3] R.W. Eason (Ed.), Pulsed Laser Deposition of Thin Films: Applications-Led Growth of Functional Materials, John Wiley & Sons, New York, 2006.

[4] M. Morcrette, P. Barboux, J. Perriere, T. Brousse, A. Traverse, J.P. Boilot, Solid State Ionics 138 (2001) 213–219.

[5] M. Morcrette, P. Barboux, J. Perriere, T. Brousse, Solid State Ionics 112 (1998) 249–254.

[6] C. Julien, E. Haro-Poniatowski, M.A. Camacho-Lopez, L. Escobar-Alarcon, J. Jimenez-Jarquin, Mater. Sci. Eng. B: Solid State Mater. Adv. Technol. 72 (2000) 36–46.

[7] A. Rougier, K.A. Striebel, S.J. Wen, T.J. Richardson, R.P. Reade, E.J. Cairns, Appl. Surf. Sci. 134 (1998) 107–115.

[8] S. Higuchi, I. Tsukada, Japanese J. Appl. Phys. Part 2: Lett. 42 (2003) L1066–L1068.

[9] I.P.K. Carruthe Jr, L.W. Stulz, Appl. Opt. 13 (1974) 2333–2342.

[10] F.J. Gordillo-Vazquez, J. Appl. Phys. 90 (2001) 599–606.

[11] M.F. Zhou, Z.W. Fu, L.N. Zhang, Q.Z. Qin, Chem. Phys. Lett. 318 (2000) 644–648.

[12] S. Amoruso, M. Angeloni, G. Balestrino, N. Boggio, R. Bruzzese, P.G. Medaglia, A. Tebano, M. Vitiello, X. Wang, Appl. Surf. Sci. 247 (2005) 64–70.

[13] T. Dumont, T. Lippert, M. Dobeli, H. Grimmer, J. Ufheil, P. Novak, A. Wursig, U. Vogt, A. Wokaun, Appl. Surf. Sci. 252 (2006) 4902–4906.

[14] P.T. Mannion, S. Favre, C. Mullan, D.S. Ivanov, G.M. O'Connor, T.J. Glynn, B.P. Doggett, J.G. Lunney, J. Phys. (Conf. Ser.) 59 (2007) 753–757.

[15] B. Toftmann, J. Schou, T.N. Hansen, J.G. Lunney, Phys. Rev. Lett. 84 (2000) 3998–4001.

[16] A. Keith Brewer, P.D. Kueck, Phys. Rev. 46 (1934) 894.

[17] T. Whitmore, personal communication, Hiden Analytical, UK, 2007.

[18] T.N. Hansen, J. Schou, J.G. Lunney, Appl. Phys. Lett. 72 (1998) 1829–1831.

[19] R.F. Wood, J.N. Leboeuf, D.B. Geohegan, A.A. Puretzky, K.R. Chen, Phys. Rev. B 58 (1998) 1533–1543.

[20] D.W. Koopman, D.A. Tidman, Phys. Rev. Lett. 18 (1967) 533.

[21] R. Jordan, D. Cole, J.G. Lunney, K. Mackay, D. Givord, Appl. Surf. Sci. 86 (1995) 24–28.

[22] P.C. Zalm, J. Vacuum Sci. Technol. B 2 (1984) 151–152.

[23] E. Vanderiet, J.C.S. Kools, J. Dieleman, J. Appl. Phys. 73 (1993) 8290–8296.

[24] L.S. Dorneles, D. O'Mahony, C.B. Fitzgerald, F. McGee, M. Venkatesan, I. Stanca, J.G. Lunney, J.M.D. Coey, Appl. Surf. Sci. 248 (2005) 406–410.

[25] D.R. Lide, Handbook of Chemistry and Physics, CRC, New York, 1998.

[26] G. Rog, W. Kucza, A. Kozlowska-Rog, J. Chem. Thermodyn. 36 (2004) 473–476.

[27] J.B. Malherbe, S. Hofmann, J.M. Sanz, Appl. Surf. Sci. 27 (1986) 355–365.

[28] T. Dumont, Laser Interaction with Materials: From Transparent Materials to Thin Films, PhD Thesis, ETH, Zurich, 2006.

[29] F.J. Gordillo-Vazquez, C.N. Afonso, J. Appl. Phys. 92 (2002) 7651–7657.

[30] L. Andrews, W. Saffell, J.T. Yustein, Chem. Phys. 189 (1994) 343–349.

[31] J.A. Chaos, R.W. Dreyfus, A. Perea, R. Serna, J. Gonzalo, C.N. Afonso, Appl. Phys. Lett. 76 (2000) 649–651.