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Luminescence characterization of ultrathin MgO films of high crystallinity prepared by pulsed laser deposition

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Abstract Thin MgO films with thicknesses ranging from 127 to 35 nm were prepared by pulsed laser deposition on Si substrates. The crystalline films were smooth (rms roughness 0.6–1.2 nm) with an average density of 3.5 g/cm^3. Cathodoluminescence study revealed emissions peaked at 7.65 eV and ascribed to the edge emission of large radius exciton states as well as luminescence due to the F and F^+ colour centres in the range of 2–4 eV. This luminescence is efficiently excited in the absorption band peaked at 6.2 eV and in the intrinsic absorption with the onset at 7.4 eV via energy transfer processes.

1 Introduction

Poly- and single-crystalline oxide films are of great interest for applications in photonics and optoelectronics. MgO is used as a dopant in nonlinear materials and is an important material for devices based on multilayer structures. Pure MgO is an ionic crystal with cubic fcc crystal structure (NaCl type). Single crystals of a few cm size can be grown from the melt by the arc fusion growth method [1] at 2,850 °C, which sets certain limits on their purity and defectness. Platelets cleaved from such oriented single crystals often serve as substrates for growth of epitaxial layers from other materials. Technologically advanced Si wafers have attracted attention as substrates for thin multilayer devices. However, in order to passivate the Si surface and to reduce the mismatch of lattice constants buffer, oxide layers like MgO have to be used. Various methods for synthesis of nanosized crystals and the deposition of thin films of MgO have been developed (see [2]). It has been shown that pulsed laser deposition (PLD) allows convenient preparation of high quality MgO films with a smooth and defect-free surface [2]. The aim of the present work was the characterisation of the properties of ultrathin MgO films grown by PLD from high quality single crystal targets. A comparison of luminescence properties of the PLD films and MgO crystals was carried out in order to understand the behaviour of electronic excitations and reveal their peculiarities in low dimensional systems. To the best of our knowledge, data on the luminescent properties of PLD MgO films have not been reported.

Vacuum ultraviolet (VUV) luminescence and reflection spectra of large radius Wannier excitons in pure and doped bulk MgO crystals have been investigated in detail in the energy range of 5–32 eV [3–5]. The excitation of MgO by photons with energies exceeding the band gap value of 7.8 eV results in formation of electronic excitations, which can decay radiatively. Emission of near edge luminescence of large radius free excitons (FEs) is detected at 7.65 eV, which decay time lies in the sub nanosecond range. The influence of isoelectronic Ca^{2+} impurities in MgO and the resulting change in luminescence has been investigated in [5]. Effects induced in the optical spectra by heterovalent impurities-defect complexes (M^{3+} + cation vacancy + hole, being known as V_M-bands), which require charge compensation, have been analysed in [6]; the role of intrinsic colour centres (F, F^+) was studied in [7]. Recently it has been shown that surface morphology plays an important role in the formation of optical properties of pure and mixed MgO–CaO nanocrystals prepared by chemical vapour deposition [8, 9]. In the case of our thinnest PLD films, the size of crystallites can be in the range where analogous effects may become observable.

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2 Experimental details

The PLD setup used in thin film preparation has been described earlier [10]. The deposition conditions of the films were as follows: laser wavelength 248 nm, laser pulse energy density on the target 7 J/cm^2, repetition rate of laser 10 Hz, substrate temperature 580 °C, and oxygen pressure in the chamber 0.002 mbar. At these conditions, films with a high degree of crystallinity and with very smooth surfaces were obtained on Si substrates. By varying the number of laser pulses on the target, films with different thickness were grown. A plate cleaved from high quality MgO single crystals grown by the arc-fusion method was used as a target [1]. Structural and morphological characterisation of the films was also performed by XRD, XRR methods and AFM. The respective data for films with different thickness are collected in Table 1.

Low temperature cathodoluminescence experiments were performed using tunable electron beam excitation in the range of 1–30 keV, which allows adjustment of the penetration depth of exciting electrons in accordance with the film thickness. Luminescence was analysed by two double monochromators, which cover the range from 4.5–11.5 eV (vacuum grating monochromator) and 1.7–6 eV (UV-visible prism instrument), respectively. Low temperature time resolved photoluminescence study under synchrotron radiation excitation in the VUV region was carried out at SUPERLUMI station of HASYLAB at DESY [11]. The emission and excitation spectra were recorded in time-integrated mode and within time windows with a selected length Δt and a delay δt in respect of the arrival of the excitation pulse. All films described in Table 1 were investigated by luminescence methods yielding similar spectroscopic results. Therefore film no. 111 with 55 nm thickness was selected as a typical representative of the whole set.

3 Results and discussion

Figure 1 shows a typical AFM image of the smooth surface of the MgO films. According to Table 1, the highest achieved surface root-mean-square roughness of the films was 0.6 nm (XRR), which is even better than the results of Ref. [2] (0.82 nm) reported for MgO deposition under optimised conditions. The film densities are close to the theoretical value of 3.58 g/cm^3, which indicates high crystallinity. This was confirmed with the XRD results, where the MgO (200) diffraction peak was observed. The growth rate increases with the thickness of the films. The XRR analysis also suggests that an interface layer of a few nm thickness was also formed on top of Si substrate.

Table 1 Properties of MgO films evaluated by the XRR method

Sample	Number of laser pulses	Film thickness nm	Film density g/cm^3	Film roughness nm
110	25,000	127	3.4	0.8
112	17,000	79	3.57	0.6
111	12,500	55	3.46	0.6
113	9,000	35	3.50	1.2

Figure 2a presents the cathodoluminescence spectrum of a high purity MgO crystal at 5 K, and panel (b) shows typical spectra recorded from thin MgO films at 5 K and 293 K. The narrow line at 7.65 eV corresponds to edge emission due to large radius exciton states as discussed earlier in [4, 5] for pure and Ca-doped MgO crystals. The decay time of the main emission component of the free exciton is very fast with $\tau < 200$ ps, which is typical for singlet emissions [12]. Based on the analysis of the reflection spectra, it has been shown in [13] that the order of excitonic states in MgO is inverted. A comparable situation was observed also for BeO and ZnO [14]. Therefore, the non-radiative relaxation from the triplet to singlet states depopulates the former ones and only fast singlet emission is observed in accordance with the observed decay kinetics of edge emission. Doping with isoelectronic impurities like Ca^{2+} ions induces mixing of the states, which results in the redistribution of intensities between different components and the appearance of longer components with ns duration [15]. In the UV range, an emission band peaked at 5.3 eV is observed, arising from the recombination of electrons and holes at the vicinity of V_{Al} centres, that consists of cation vacancies near Al^{3+} ions (introduced as unintentional impurity) [6]. The broad band covering the range of 2–4 eV is a result of superposition of luminescence of F- and F^+ centres [7] with emission maxima at 2.4 and 3.15 eV, respectively. The band peaked at 2.85 eV is revealed in crystals with internal stress as reported in [16]. Also the effects of irradiation, thermo-chemical treatment and the influence of H impurities on the emission spectra have been analysed earlier using the time resolved spectroscopy, and our experimental results are in a good agreement with the observation reported in [17].

The integral intensity of cathodoluminescence from MgO films, with some variation from sample to sample, is about two orders of magnitude weaker than that obtained from the single crystals. The dominating luminescence bands are located in the visible spectral region. Nevertheless, as shown in Fig. 2b, we were able to reveal the edge emission from the MgO films. Analogously to the single crystals at 5 K, it is a narrow line peaked at 7.65 eV, whereas at room temperature a more complex structure appears extending to lower energies. This can be explained as a superposition of phonon wings and luminescence from

non-relaxed excited states. In Ref. [4] the radius of $n = 1$ Wannier excitons in MgO has been estimated to be equal to 15 Å. The detection of edge emission points to the fact that the size of crystallites in the studied PLD films has to be large enough for the existence of free excitons in the quasi 2D system. It is important to note that no UV emission bands in the region of 4–6 eV were found in the PLD MgO films. The low energy part of the spectrum at RT resembles that of the MgO single crystal at 5 K. At 5 K the luminescence spectrum of the films consists of a well pronounced band peaked at 2.75 eV and a broad structure in the region of 3–4 eV. This is a direct proof of creation of anion vacancies formed during film deposition.

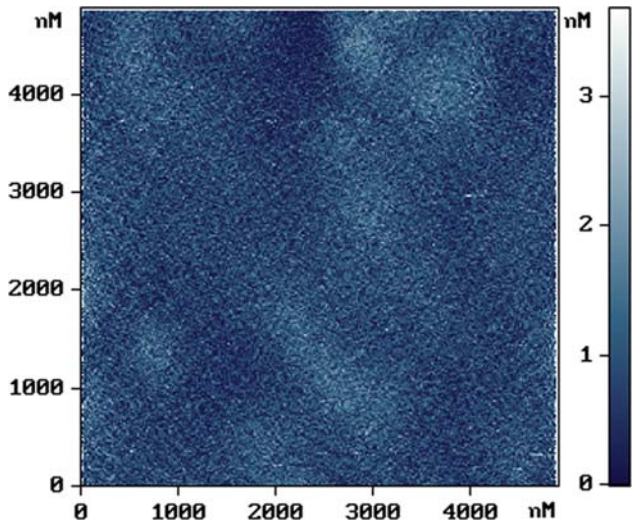

Fig. 1 Typical AFM image of a MgO film with a thickness of 65 nm on Si substrate, deposited at temperature 580 °C and 0.002 mbar of oxygen pressure

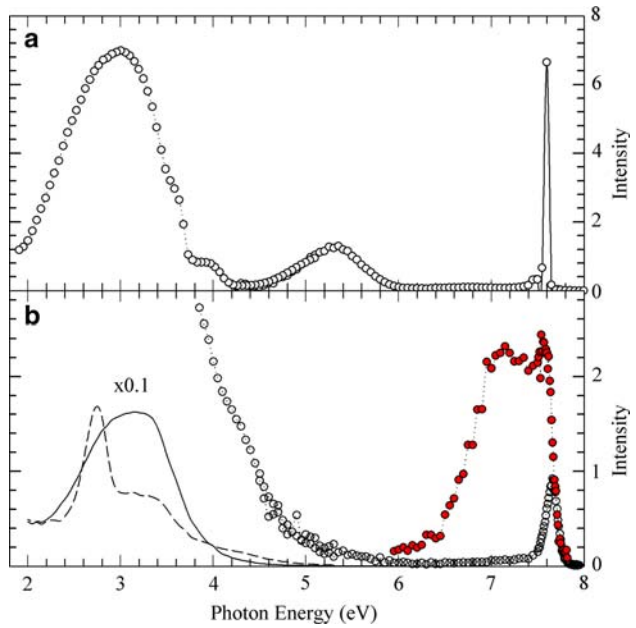

Fig. 2 (**a**) Cathodoluminescence spectra of the high purity MgO crystal at 5 K excited by 15 keV electrons. (**b**) Cathodoluminescence spectra of a MgO film (no. 111) recorded at 293 (red circles and solid line) and 5 K (open circles and dashed line). Energy of exciting electrons was 1 keV and the beam current 1 μA. The intensity in the low energy part of both spectra at 293 K is scaled in order to visualize the high-energy part in more detail (the absolute value of intensity for VUV emission at 293 K is approximately 10 times smaller than that at 5 K)

In comparison with cathodoluminescence studies, photoluminescence spectroscopy is a significantly more sensitive and selective method in order to investigate properties of electronic excitations. Figure 3 presents the results of photoluminescence studies using synchrotron radiation excitation. The luminescence spectrum of MgO films excited by 5.9 eV photons is nearly elementary, practically consisting of a dominating single gaussian band. The fit of the fast emission component (see Fig. 3 captions for details) resulted in parameters ($I_{max} = 3.15$ eV and FWHM 0.74 eV) close to those reported for the F^+ band under intra-centre excitation [7]. Additional support comes from the decay measurements of this emission, which can be approximated by single exponential with a characteristic time of 3.7 ns without any significant long components in the range of 200 ns (see inset of Fig. 3). This is in a good agreement with spectroscopy of F^+ centres in other metal oxides like BeO ($\tau \leq 1$ ns) and Al_2O_3 ($\tau \leq 2.2$ ns) [18]. Much slower decay components extending over 8 decades from 20 ns to 2 s have been reported for MgO single

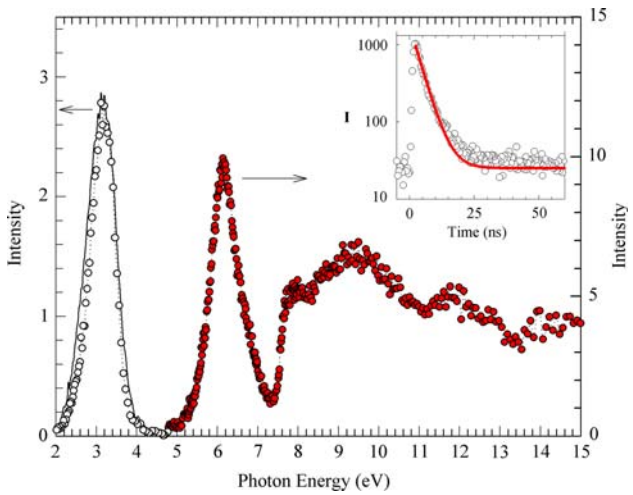

Fig. 3 Photoluminescence emission and excitation spectra of MgO film (no. 111) recorded under synchrotron radiation excitation at 9 K. Luminescence was excited by 5.9 eV photons and recorded for the time integrated signal (solid line) and in a short time-window (δt 2 ns and Δt 22 ns). The excitation spectrum was recorded for the time integrated 3.1 eV emission (red circles). The inset shows the decay (open circles) of 3.1 eV emission excited by 5.9 eV photons. The red solid line presents the result of the fit using a single exponential function

crystals [17]. In the same paper it was concluded that charge trapping and transport govern the decay kinetics, even though from the selection rules much shorter lifetimes can be expected. Obviously, the thin MgO films have an advantage over impurity, defect, and trap rich single crystals as suitable samples for revealing intrinsic dynamics of electronic excitations. It is interesting to note that the main overlapping absorption bands have been reported for the F^+ and F centre with maxima at 4.96 and 5.03 eV, respectively [7]. Our MgO films exhibit the first strong excitation band at 6 eV. It is obvious that this excitation band cannot be due to the higher excited states of F^+ and F centres, while the first excitation bands in UV, with an oscillator strength as high as 0.7 for latter one [7], do not contribute strongly to the F^+ luminescence. On the other hand, since only the F^+ emission is detected under photoexcitation in this band, it is unlikely to be due to impurity absorption. It is possible that this absorption in the films is related to already existing anion vacancies, which form F^+ centres in an excited state after attracting an electron. In alkali halides such centres are well known and thoroughly studied (see e.g. [19]). However, it cannot be excluded that more complicated defects like bivacancies are responsible for this band, whose origin is a subject for further studies. The luminescence of F^+ centres is also efficiently excited through energy transfer processes by electron-hole pairs in the region of intrinsic absorption of MgO above 7.7 eV. The only additional luminescence band (not shown) found under such excitation in the MgO films stems from to Cr^{3+} centres with the main emission line at 717 nm [20]. A very low concentration (typically $\leq$10 ppm) of Cr^{3+} results from unavoidable residual impurities in the target crystals and chemicals used in their growth.

Both cathodoluminescence and photoluminescence emission spectra recorded from PLD films cover the spectral region of MgO nanocrystal luminescence, where two weak emission bands at 3.4 and 3.3 eV have been revealed and assigned to radiative recombination process at surface anions of different morphology [9]. However, probably due to competition with other much stronger radiative decay channels, we failed to reveal the respective excitation bands peaked at 4.6 and 5.5 eV according to Ref. [9]. Hence, the presence of luminescence from surface sites of MgO nanocrystallites in PLD films requires further investigation.

The major difference between cathodoluminescence spectra of the studied PLD films and MgO single crystals is the absence of emission from V_M-type of centres (bands in the region of 4–6 eV). This raises question whether the cation vacancies are not present at all in the PLD films. However, a significant amount of anion vacancies contributing to the formation of F-type centres and efficient transfer of a small quantity of unintended impurities from the target crystal to all PLD films suggest another possibility. Taking into account that the thicknesses of all films studied are below the diffusion length of free carriers ($L = 220$ nm) reported in [21] for MgO, it becomes obvious that non-radiative recombination at the surface plays an important role for ultrathin films. This is obviously the main reason for the absence of luminescence from V_M-type centres. In principle, also the free excitons in MgO are very mobile, but their lifetime compared to that of the recombining electron-hole pairs at the V_M-centres is much shorter. Accordingly, the diffusion length $L = (D\tau)^{1/2}$, where D is diffusion coefficient, is much smaller for free excitons with a very short lifetime τ. Thus, influence of near-surface losses on the edge emission is expected to be much weaker, which makes its observation possible.

4 Conclusions

Ultrathin and smooth MgO films were prepared using the PLD method, and their luminescence properties were investigated for the first time. In all PLD films, the luminescence of colour centres (F and F^+) in the visible region as well as that of large radius excitons in the VUV region was detected. This suggests for presence of anion vacancies formed during sample preparation as well as large areas of 'defectless' crystal lattice with the translational symmetry required for formation of free excitons. To our surprise practically no luminescence from the V_M-centres in the UV region was detected. This was explained by the diffusion of free charge carriers, which is large enough in comparison with the film thickness to allow their efficient movement onto the surface. Thereafter non-radiative recombination processes at surfaces play an important role in ultrathin MgO films. Finally, we have shown that the luminescence methods are useful in characterization of properties of electronic excitation and their dynamics in thin films.

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