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VUV spectroscopy and electronic excitations in nano-size alumina

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ABSTRACT

Luminescence properties and electronic excitations of δ - and Θ -phases of Al_2O_3 nano-powders, prepared by plasma processing technique, were studied using time-resolved luminescence spectroscopy under vacuum ultraviolet excitation. The fundamental absorption edge was found at 7.5 eV, which is 1.5 eV less than that of α - Al_2O_3 in agreement with theoretical predictions for transition alumina. The broad-band emissions with maxima at 5.5 and 4.6 eV are assigned to radiative decay of the intrinsic excitations. Emission of transition metal impurities was found near 1.75 eV. The emission bands peaked at 3.1 and 2.6 eV are assigned to F^+ and F centres, respectively.

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1. Introduction

Alumina is widely used technological material in the form of ceramics or single crystals. The electronic properties of its stable α -phase have been thoroughly investigated (Valbis and Itoh, 1991; Kirm et al., 1999). The metastable polymorphs (β , γ , δ , Θ , etc.) known as transition alumina have mainly found theoretical attention. Various physical properties of transition alumina have been evaluated theoretically (e.g. Lee et al., 2007; Ching et al., 2008). In α - Al_2O_3 all Al ions have octahedral coordination (AlO_6), whereas in transition aluminas some of them are tetrahedrally coordinated (AlO_4). The number of occupied tetra- or octahedral sites varies for different polymorphs, which leads to remarkable differences in their properties. There are only a few experimental reports on intrinsic electronic properties obtained for δ - Al_2O_3 powder (Kirm et al., 2005) or for mixed amorphous-crystalline Al_2O_3 films (Aarik et al., 2005). Luminescence properties of γ - and δ - Al_2O_3 nano-powders have been evaluated in Gorbunov et al. (2005) and nano-ceramics in Kortov et al. (2008). The main goal of our work was to investigate the electronic properties of the δ - and Θ -phases of alumina and comparison of properties with the α -phase. Also effects due to size of particles may influence optical properties of nano-powders.

2. Experimental details

The plasma processing technique (Palcevskis et al., 2001) was used to prepare nano-powders from the raw alumina of 99.7% purity. Various structural (XRD) and morphological characterization (AFM, TEM) methods were applied. The alumina powder was in the mixed δ -, Θ - Al_2O_3 crystallographic phase with spherical particle shape of 75 and 40 nm average size (specific surface area 20 and 50 m^2/g , respectively). Low temperature time-resolved VUV spectroscopy with synchrotron radiation (SR) was performed at the SUPERLUMI station (Zimmerer, 2007). Simultaneously with time-integrated (TI) luminescence, spectra in two time windows with the length of Δt and delayed by δt relative to the exciting SR-pulse were registered. The cathodoluminescence (CL) study was performed in Tartu. The CL spectra were corrected to the spectral transmission of the detection channel.

3. Results and discussion

As shown in Fig. 1a the electron beam excitation results in several overlapping emission bands with maxima at 5.5, 4.5, 3.3 and 2.2 eV. Selective excitation by 4.1 eV photons reduces a number of bands and the main luminescence maximum is near 3 eV. In time-resolved spectra fast nanosecond and considerably slower microsecond components were found at 3.1 and 2.6 eV, respectively. Increase of exciting photon energy to 8.27 eV adds luminescence bands in the UV region (Fig. 1b,c). There is always present an emission near 1.7 eV with a long decay time.

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Fig. 1. (a) Cathodoluminescence spectrum (1) of nano-alumina (20 m²/g) at 5 K and its VUV-UV part (1') recorded through a double prism and vacuum monochromator, respectively. The signal intensities of the spectra were adjusted in the overlapping 5.0–5.2 eV region of both monochromators and the curve (1') is increased by a factor of 5 in order to visualize short-wavelength emissions. Emission spectra of the same sample at 8 K excited by 4.1 eV photons of TI (2), fast (3, $\delta t = 5.5$ ns, $\Delta t = 55$ ns) and slow components (4, $\delta t = 61$ ns, $\Delta t = 109$ ns). The intensity of latter curve (4) is multiplied by 10. (b) Emission spectra of nano-alumina (20 m²/g) at 10 K. TI emission excited by 8.27 eV photons (4), TI (5) and slow ($\delta t = 85$ ns, $\Delta t = 77$ ns) component (6) excited by 7.09 eV photons. (c) Emission spectra of nano-alumina (50 m²/g) at 10 K. TI (7) and fast ($\delta t = 1.8$ ns, $\Delta t = 13.9$ ns) component (8) excited by 8.27 eV photons and TI emission excited by 16.5 eV photons (9).

Fig. 2 demonstrates high-resolution emission spectra of the 1.7 eV band of both samples at 8 K. The narrow lines starting from 680 nm are followed by a broad wing extending until 900 nm, which is typical for transition metal impurity emissions. It has been reported in Monteiro et al. (2002) that in this spectral region the $^4T_1 \rightarrow ^6A_1$ transition of $Fe^{3+}d^5$ configuration occur in $\alpha-Al_2O_3$, being also identified in nano-structured alumina (Mo et al., 1994). However, R_0 doublet (the $^2E \rightarrow ^4A_2$ transition of $Cr^{3+}d^3$ configuration) have been reported at 682.6 and 685.9 nm (Snytnikov et al., 2008). The positions are practically coinciding with the first two lines in Fig. 2 found at 682.2, 685.7, 688.7 and 691 nm. This indicates the presence of Cr^{3+} ions substituted to different Al^{3+} sites or in different phases of nano-alumina. The interaction of octahedrally coordinated Cr^{3+} ions with Fe^{3+} impurities leads to the formation of an emission band at 770 nm (Snytnikov et al., 2008), which partly explains the origin of the long-wavelength wing. The presence of Ti^{3+} ions with broad-band luminescence at 750 nm is less probable.

Fig. 3 shows excitation spectra, where the main feature is a notable excitation onset at ~ 7.5 eV observed for all emissions. It is also in agreement with earlier results (Kirm et al., 2005; Aarik et al., 2005; Gorbunov et al., 2005). This onset is assigned to the beginning of intrinsic absorption of transition alumina. Theoretical studies predict also the reduction of energy gap in a row of $\alpha > \kappa > \Theta > \gamma$ alumina from 6.72 to 4.40 eV (Lee et al., 2007). It is caused by the formation of additional sub-bands on the top of the valence band

Fig. 2. High-resolution emission spectra of alumina nano-powders (20 and 50 m²/g; 1, black; 2, blue lines, respectively) at 8 K excited by 8.3 eV photons. The spectra were recorded using a CCD camera with the spectral resolution of 1 nm.

due to nonbonding oxygen orbitals in oxides (Mürk, 1997). In transition alumina also a downshift of conduction band bottom occurs caused by change of potentials due to shorter Al–O bond distances of Al^{3+} ions in tetrahedral coordination (Lee et al., 2007).

Two types of self-trapped excitons (STEs) have been revealed in $\alpha-Al_2O_3$ with nanosecond emissions at 7.6 and 3.7 eV (Kirm et al., 1999). The shrinkage of the energy gap by ~ 1.8 eV of transition alumina also influences the energetic positions of relaxed excited states. UV emission bands are efficiently excited at energies above 7.5 eV, which allows us to assign those to intrinsic ones. The 5.5 eV band is due to singlet STE emission with nanosecond decay kinetics (not shown, two decay components $\tau = 2.2$ ns and 13.3 ns) being an analogue of 7.6 STE emission of $\alpha-Al_2O_3$. The 4.6 eV emission has considerably longer decay time. The 4.3 eV emission with microsecond duration was also observed from nano-ceramics (Kortov

Fig. 3. Excitation spectra of nano-alumina (a,b, 20 m²/g; c, 50 m²/g) at 8 K. (a) TI 4.43 eV emission (triangles), TI 3.1 eV emission (solid blue line) and its slow component (circles, $\delta t = 61$ ns, $\Delta t = 109$ ns). (b) TI 1.75 eV emission (dashed green line), TI 5.5 eV emission (black line) and its slow component (circles, $\delta t = 85$ ns, $\Delta t = 77$ ns). (c) 4.43 eV emission (circles), 3.1 eV emission (solid blue line) and 1.75 eV emission (dashed green line) all recorded in TI mode.

et al., 2008). Therefore, the 4.6 eV band can be either due to triplet STEs or recombination of electrons and holes near some defect or optically inactive impurity centre.

In the transparency region (<7.5 eV), there is a competition between defect and impurity absorption as the excitation spectra of various centres behave oppositely (Fig. 3a,b). In α -Al₂O₃ (Valbis and Itoh, 1991) the presence of F⁺- and F-centers is well established, emitting at 3.8 and 3.0 eV with decays of 2.1 ns (Surdo et al., 2001) and 36 ms (Lee and Crawford, 1979), respectively. The 3.1 eV emission of transition alumina has also a lifetime in the few nanosecond range ($\tau_1 = 2.7$ ns and $\tau_2 = 12.5$ ns) and its excitation spectrum consists of 3 peaks, typical for the transparency range of defect rich α -Al₂O₃. This 3.1 eV luminescence in our samples originates from F⁺ centers. Earlier the 3.2 eV emission in alumina nano-powders was assigned to the surface F⁺ centers (Gorbunov et al., 2005). The 2.6 eV emission with a long decay is tentatively assigned to F-center luminescence.

Our study did not reveal any significant effects of particle size, which is obviously too large to see any quantum confinement in wide gap insulators with small radius electronic excitations. The main effect observed was the decrease of luminescence intensity because of rising contribution of non-radiative processes on surfaces. The spectral features in the luminescence of 50 m²/g alumina samples are influenced by inhomogenous broadening effects.

In conclusion the luminescence properties of mixed δ -, Θ -Al₂O₃ nano-powders were investigated and luminescence bands due to intrinsic excitations, colour centers and transition metal ions identified.

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