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2001 J. Phys.: Condens. Matter 13 8931

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Radiation induced recombination processes in AlN ceramics

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Received 2 May 2001

Published 20 September 2001

Online at stacks.iop.org/JPhysCM/13/8931

Abstract

Luminescence processes are studied for aluminum nitride, AlN, ceramics after exposure to ionizing radiation and ultraviolet radiation (UVR) using the methods of photoluminescence (PL), optically stimulated luminescence (OSL) and thermoluminescence (TL). The luminescence processes are explained in terms of radiation-induced charge transfer and radiative recombination of the donor–acceptor pairs, based on oxygen-related defects of the AlN crystalline lattice. The comparative effects of the two types of radiation, the efficiency of TL and OSL and the optimal sintering procedure of the ceramics are discussed for an AlN ceramic proposed for potential application in dosimetry.

1. Introduction

Aluminum nitride, AlN, is known mostly because of its application in microelectronics as a substrate material. Our recent papers [1–3] were devoted to studies of AlN ceramics as potential material for application in ionizing radiation and ultraviolet radiation (UVR) dosimetry using the methods of thermoluminescence (TL) and optically stimulated luminescence (OSL).

It was found, in [1], that after exposure to ionizing radiation AlN ceramics demonstrate the following dosimetric properties. The TL signal is characterized by a structureless glow curve peaking near 300 °C, a very high sensitivity, a five decade wide linear dynamic dose range, good repeatability of measurements and a minor influence of the heating rate on the TL signal. The OSL signal was found to be much weaker than the TL response.

The properties of AlN ceramics after exposure to UVR were studied mainly qualitatively using the dosimeter material Al₂O₃:C for comparative measurements [3]. It has been shown that a very high yield and linear dose response characterize the UVR-induced TL from AlN–Y₂O₃. It was found that this material has a spectral sensitivity in a broad region from 200 to 360 nm, covering almost the whole UVR spectrum. In the 280–320 nm spectral range, which is potentially harmful for human beings, the material demonstrated spectral sensitivity

similar to that of human skin. This property allows one to regard the material as a potential detector for personal UV dosimetry.

However, a practical application of the AlN ceramics for dosimetry is hampered by the serious disadvantage of the material—the high fading rate of the TL and OSL signals after exposure to radiation during storage at room temperature. The measures undertaken to control the fading process helped to reduce the process to a definite extend but not to eliminate it [2].

The aim of the present work is the study of the processes of radiation-induced charge transfer and recombination luminescence in the material, the study of the peculiarities of TL and OSL signals and the search for methods for their stabilization.

2. Materials and equipment

Samples of AlN high-density ceramics were prepared in the Institute of Inorganic Chemistry, Latvia, by sintering at high temperatures (1640–1785 °C) from fine AlN and Y₂O₃ powders produced by plasma synthesis [4]. The Y₂O₃ powder was used as a sintering aid; its concentration varied in the 0–9 wt% range. The grown polycrystalline ceramic cylinders were cut into 1 mm thick tablets.

The optimal dosimetric properties were shown by the sample AlN-181 (with 3.8 wt% of Y₂O₃) sintered at 1785 °C for 120 min and characterized with an oxygen content of 0.36 at%. AlN ceramics is a light-sensitive material; during irradiation, storage and measurement the samples were protected from the uncontrolled influence of ambient light.

All TL and some of the OSL measurements were made using a Risø model TL/OSL-DA-12 reader with linear planchet heating and equipped with a built-in ⁹⁰Y/⁹⁰Sr software-controlled beta source and a powerful blue LED array (470 nm) for OSL stimulation [5, 6]. Most of the UV irradiations were made using a metal halide lamp, type Sol 2 manufactured by K Honley GmbH. Photoluminescence (PL) and OSL spectra were also measured (in Latvia), using a deuterium lamp LDD-400 and a grating monochromator MDR-2 for excitation and a 500 W halogen lamp with a yellow filter ($\lambda > 470$ nm) for stimulation.

3. Experimental results

3.1. Spectral characteristics of recombination luminescence of AlN

AlN is a wide band gap (6.2 eV) material with the wurtzite structure [7], exhibiting a large affinity for oxygen. As a natural dopant an oxygen ion substitutes for nitrogen in regular lattice sites during the growing of AlN crystals. It was found [8] that the presence of the oxygen impurity is responsible for a wide luminescence band in the UV–blue spectral region. It rises in samples of all origins, under exposure to both ionizing radiation and UVR. The particular spectral position and intensity of the wide luminescence band depends on the oxygen concentration in the AlN lattice of the sample.

The spectral characteristics of the AlN-181 sample used in our work were obtained under UVR at room temperature. Under these conditions the PL spectrum contains at least three bands: an oxygen-related UV–blue band and 600 nm and 1000 nm bands. To simplify the picture, the long-wavelength bands are not shown in the spectrum since they will not be discussed here. Monitoring the UV–blue luminescence band during steady-state UV irradiation, it was found that the intensity of the luminescence increases during 30–40 min until saturation, while the peak position shifts from 360 nm at the very beginning of the exposure (figure 1, curve 3) to 385 nm at the moment of saturation (curve 4). After switching off the excitation radiation an afterglow is observed with a luminescence band peaking at 390 nm (curve 5) and a decay time of minutes. (A similar band position is observed under

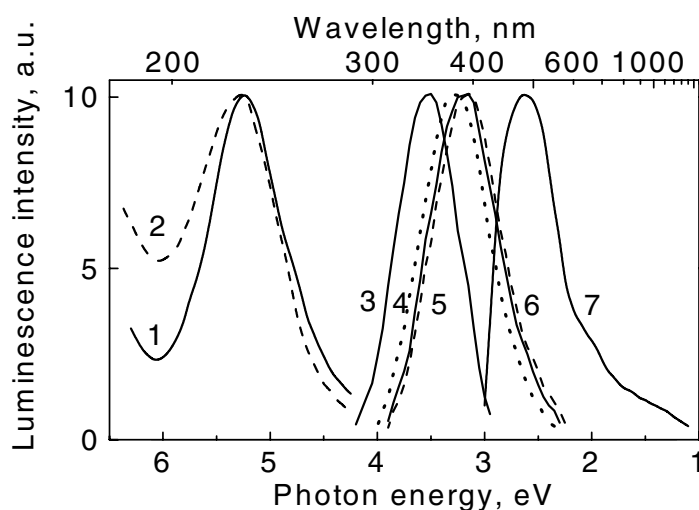


Figure 1. Spectral properties of AlN ceramics (AlN-181) at room temperature: 1, excitation spectrum of the UV–blue PL band; 2, OSL excitation; 3, PL at the very beginning of the irradiation with $\lambda = 240$ nm; 4, PL after 60 min of continuous irradiation with $\lambda = 240$ nm; 5, OSL emission spectrum; 6, afterglow luminescence; and 7, OSL stimulation spectrum.

x-ray irradiation [2].) The excitation spectrum of the UV–blue luminescence is characterized by a well pronounced band at 240 nm (curve 1) on the extended tail of the absorption edge [8].

Such spectral characteristics can be explained in terms of the idea [9] of recombination luminescence with participation of the oxygen-related defects. Using electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) methods a recent paper [10] has proved that two types of oxygen-related centres are responsible for the UV–blue luminescence. One of them involves an oxygen ion substituting for a nitrogen ion on a regular lattice site O_N , and the other is a (O_N-v_{Al}) complex defect, formed from O_N and a neighbouring aluminium vacancy v_{Al} . Exposure of the material to radiation results in charge transfer between the defects of the different types forming a donor ($(O_N)^-$ i.e. an electron trapped on an oxygen impurity, which substitutes for a nitrogen on a regular lattice site) and an acceptor ($(O_N)^+-v_{Al}$ i.e. a hole trapped on a complex defect) pair with different separation distances. The close donor–acceptor pairs recombine during the irradiation process producing the UV–blue luminescence. The afterglow luminescence shortly after terminating the irradiation corresponds to recombination between similar, but more distant, pairs.

The donor–acceptor pairs with larger separation survive (forming a stored light sum, i.e. stored integrated light signal) until their recombination is initiated (and the stored light sum released) by heating or illuminating the sample with visible or infrared light, producing TL or OSL, respectively. The luminescence band of the OSL (curve 6) practically coincides with the afterglow luminescence band (curve 5), the luminescence of TL is also very close to these bands [1]. This fact indicates that the stimulated luminescence arises due to recombination of the same donor–acceptor pairs.

The OSL process is characterized also by OSL excitation (the OSL yield versus UVR wavelength) and stimulation (the OSL yield versus visible–infrared illumination wavelength) spectra. The OSL excitation spectrum (curve 2) coincides with the PL excitation band. We ascribe this band at 240 nm to light absorption by the O_N-v_{Al} centre, with its subsequent ionization and charge transfer. The stimulation spectrum (curve 7) after UVR covers the

400–1200 nm region with a pronounced maximum around 500 nm. A similar stimulation spectrum was obtained after exposure to ionizing radiation [2].

3.2. Effect of the type of radiation on TL and OSL signals

The stimulated luminescence processes in AlN samples were investigated using both UV and beta irradiations. Figure 2 demonstrates the TL curves from the same AlN sample after exposure to ionizing radiation (curve 1) and UVR (curve 2). In both cases the TL signal is characterized by a very broad and structureless glow curve, the UVR-induced TL curve is shifted to a significantly higher peak temperature (320 °C) compared to the beta-induced TL curve (260 °C). In all cases the stored light sum is subject to fading. The high-temperature part of the glow curve is the most stable during storage and shows less fading [1]. Lower fading of the integrated TL signal was observed for AlN samples exposed to UVR (40% fading over 24 h of storage) than for samples exposed to beta radiation (66% fading). This is explained by the shift of the TL glow curve to a higher temperature.

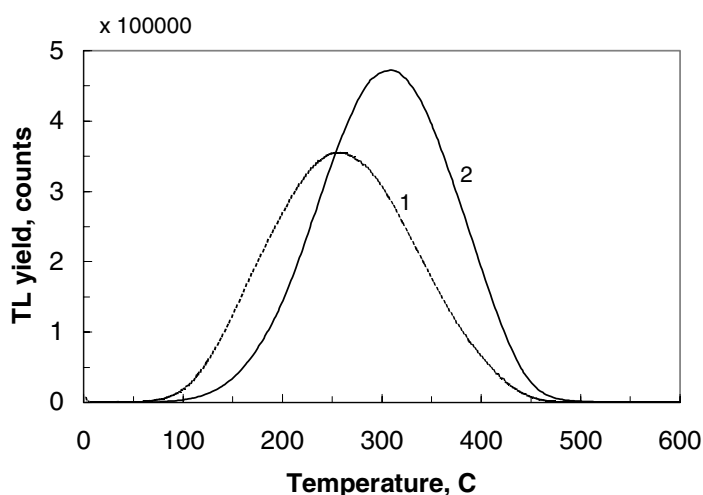


Figure 2. TL curves of AlN-181 after irradiation with a 100 mGy beta dose (curve 1) and 1 min exposure to UVR (using the Sol2 device + glass filter with peak transmission at 350 nm) (curve 2).

A comparison of OSL decay curves obtained from AlN after both beta and UVR irradiation is shown in figure 3. AlN appeared to have two different decay curves: (i) an intensive fast component that dominates in the beta-induced OSL curve (curve 1) and (ii) a slow component that dominates in the UV-induced OSL curve (curve 2).

It was found that the initial part of the OSL pulse, which consists mainly of the fast component, fades faster during the storage of the dosed sample than the tail of the pulse, consisting of the slow component. This is why the fading effect is higher for the beta-induced OSL, which has a dominant fast component of the decay curve: only 10% of the initial response is left after 24 h of storage. The effect of fading is less pronounced for UVR-induced OSL, having a dominant slow component: 45% of the initial response is left after 24 h.

3.3. Effect of ceramic sintering conditions

Such characteristics of stimulated processes as integrated yield and fading of the stimulated luminescence vary in a very broad range from sample to sample. We have found that the

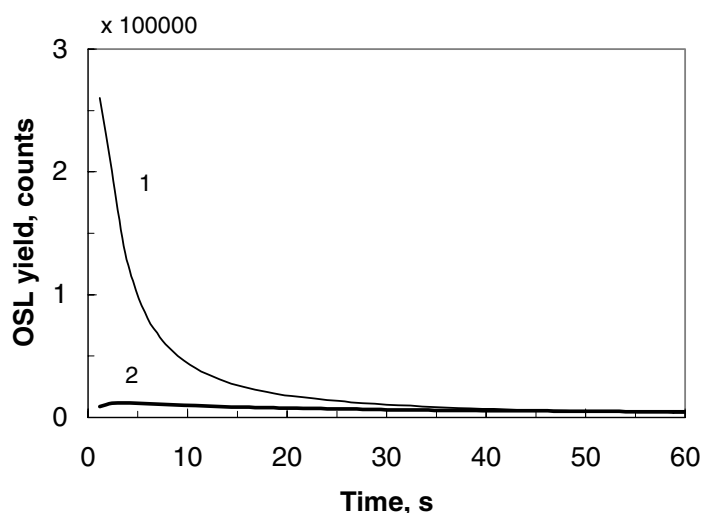


Figure 3. Blue-light stimulated OSL decay curves from AlN-181 (curve 1) and 1 min exposure to UVR (using the Sol2 device + glass filter with peak transmission at 350 nm) (curve 2).

following factors are important for production of the material with the optimal dosimetric properties: choice of the raw material for AlN powder, concentration of Y_2O_3 additive [4] and the conditions of the sintering process of the ceramics, i.e. duration and temperature. The concentration of the Y_2O_3 additive controls the number of oxygen defects in the AlN grains, with excess oxygen ions removed during the sintering process. Addition of 3.8 wt% Y_2O_3 was found to be optimal, providing the largest yield of the PL and radiation-induced stimulated luminescence.

To find out how the sintering conditions affect the beta-radiation-induced TL yield and fading rate, we studied a series of samples of the same raw composition, sintered at different temperatures in the range 1645–1780 °C (the appropriate thermal interval for production of dense ceramics with uniform distributions of AlN grains) for a constant period of time and also those sintered at constant temperature with varying sintering time. Increase of the sintering temperature leads to a shift of the TL peak position to lower temperatures and a strong increase of the TL yield (up to three orders of magnitude for some series), but also to an increasing fading rate. An increase of the sintering time at constant sintering temperature also causes a rise of the TL yield, but now the TL peak position shifts to higher temperatures while the fading rate decreases. Taking into account the observed tendencies, the optimal sintering conditions were found using the lowest possible sintering temperature and the longer sintering times.

Measuring the UVR-induced TL for the same sample series, it was found that the influence of the sintering conditions on the TL yield is not so variable—sample to sample variations are only within the range of one order of magnitude. It is important to mention here that the PL emission and excitation spectra of the samples are practically identical with only minor variations of luminescence intensity.

3.4. Peculiarities of TL and OSL methods

The use of the TL/OSL reader allowed a comparison of the properties of the materials under identical conditions. It was found that the count number of the TL integrated response is about 10 times higher the count number of the OSL response after the same dose of either irradiation

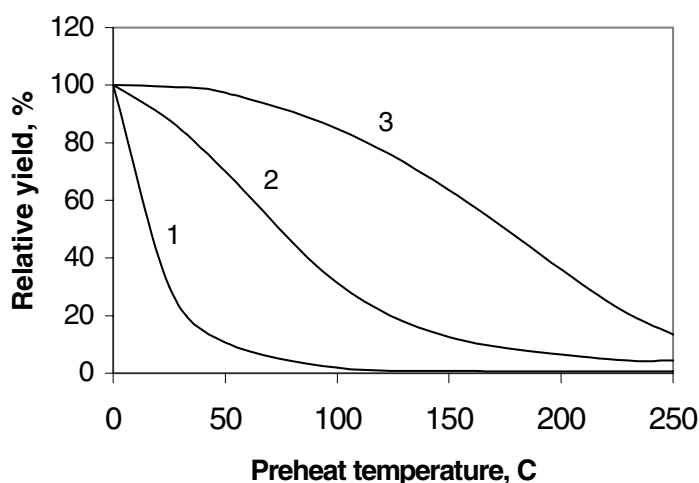


Figure 4. Preheat effect on afterglow luminescence (curve 1), OSL (curve 2) and TL (curve 3) observed in AlN-181 after irradiation with a 100 mGy beta dose. For all measurements the same 300 s long preheat procedure was applied. The curves are normalized to the values obtained without any preheat.

type. It should be mentioned that a considerable residual TL signal is still observed in the 300–500 °C region after the complete optical bleaching of the OSL signal, but no residual TL signal is observed after the complete TL reading.

A special study was performed to investigate the preheat effect on the yield of afterglow luminescence, OSL and TL. It is seen from the figure 4. that preheat up to 35 °C is enough for almost complete bleaching of the afterglow luminescence, while higher preheat temperatures are necessary to bleach the OSL signal (10% of the initial yield left at 150 °C); the TL response is even more stable (10% left at 250 °C).

4. Discussion and conclusions

The dosimetric properties of the AlN ceramics (yield and fading of stimulated luminescence) are determined by the type, amount and mutual distribution of the donor–acceptor pairs. Based on the results of our study the following stages of creation and distribution of defect centres should be mentioned.

Creation of precursor centres. Defect centres, which are precursors of the donor and acceptor centres, are created during the material production process. The origin of the AlN raw material and the concentration of Y_2O_3 determine the amount of the oxygen-related defects in the AlN grains in ceramic samples. Ceramic sintering conditions (time and temperature) affect the type, amount and topological distribution of the electron trapping centres (donor precursors); not necessarily all but at least a fraction of them are O_N centres. At the same time $O_{N-V_{Al}}$ centres, which are precursors of acceptors, are also formed.

Creation of donor and acceptor centres. The distribution of the defects, participating in the charge transfer process is determined by the type of irradiation (ionizing radiation or UVR), leading to the production of donor ($(O_N)^-$ and others) and acceptor centres ($(O_N)^+-V_{Al}$ and

light sum storage. Although the pre-irradiation distribution of precursor centres is the same, the distribution of the donors and acceptors differs depending on the type of irradiation. The results obtained include a shift of the UVR-induced TL glow curves to higher temperatures, dominance of the long-lived component in the UVR-induced OSL pulse and slower fading rates compared to beta-radiation-induced processes. They also indicate that the UVR-induced luminescence involves a larger density of deep traps than those created by beta irradiation.

Stimulation process. Comparing TL and OSL methods of releasing the stored light sum for the same sample and the same irradiation conditions, i.e. having the same distribution of donor and acceptor centres before the stimulation process, it was found that the final distribution of the stimulated charge carrier traps is determined by the method of stimulation. According to our results, the stored light sum cannot be bleached out completely by optical stimulation, the TL signal is essentially larger and thermally and temporally more stable than the OSL signal obtained under similar conditions. This leads us to conclude that optical stimulation activates only the shallowest trap levels, located in the band gap of the AlN lattice, while heating up to sufficiently high temperatures empties all the occupied trap levels.

It is not obvious that a released electron recombines immediately with an acceptor centre, a retrapping process is highly probable. We assume that the retrapping process lasts until the electron reaches the O_N centre, which is close enough to an acceptor centre, then the $(O_N)^-$ donor is formed and the process is completed by a donor–acceptor recombination process.

The fading of the stored signal is caused by the uncontrollable release of charge carriers from the trap centres and followed by a recombination process. In our opinion, only the introduction of additional dopants, providing stable deep trap levels inside the energy gap could stabilize the stored signal. The search for such impurities that improve the dosimetric properties of the material is the aim of a further study.

Recombination luminescence. The luminescence spectra of all the luminescent processes studied (the prompt luminescence, afterglow luminescence, OSL and TL) induced by exposure of the different AlN ceramic samples to both ionizing radiation and UVR have the same characteristic UV–blue luminescence band, proving that all the final luminescent processes that were mentioned are the result of recombination of the same donor–acceptor pairs. The prompt luminescence is a consequence of recombination of the closest $(O_N)^--(O_N)^+-v_{Al}$ pairs, while the afterglow luminescence, OSL and TL result from recombination of the same defect pairs with larger separation distances.

The following conclusions can be drawn.

- (1) Interconnections have been found between the dosimetric properties of AlN ceramics (yield and fading of the stimulated luminescence) and the distribution of donor and acceptor centres, the conditions of ceramic production, the type of irradiation and the method of stimulation.
- (2) Practical application of AlN ceramics for TL dosimetry of UVR seems the most promising, since the UVR-induced TL signal is the most effective and stable (compared with the UVR-induced OSL signal and the response after exposure to ionizing radiation). The optimal composition of the raw material and the optimal sintering conditions are proposed for the production of the AlN ceramics for dosimetric applications.

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