Journal of Alloys and Compounds 738 (2018) 415–421

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Thermal conductivity of rare-earth scandates in comparison to other oxidic substrate crystals

Julia Hidde [a, b], Christo Guguschev [a], Steffen Ganschow [a], Detlef Klimm [a, b, *]

[a] Leibniz-Institut für Kristallzüchtung, Max-Born-Str. 2, 12489 Berlin, Germany
[b] Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, 12489 Berlin, Germany

ARTICLE INFO

Article history:
Received 2 November 2017
Received in revised form
15 December 2017
Accepted 16 December 2017
Available online 20 December 2017

Keywords:
Oxide materials
Anisotropy
Heat capacity
Heat conduction
Calorimetry
Thermal analysis

ABSTRACT

High-temperature thermal properties of three neighboring rare-earth scandates $DyScO_3$, $TbScO_3$ and $GdScO_3$ were compared to $La_{0.29}Sr_{0.71}Al_{0.65}Ta_{0.35}O_3$ (LSAT) and sapphire. To calculate thermal conductivity, heat capacity and thermal diffusivity were measured by differential scanning calorimetry and laser flash technique, respectively. $DyScO_3$ and $TbScO_3$ showed an untypical rise in the thermal conductivity above 900 K, while for $GdScO_3$, LSAT and sapphire the expected decrease at elevated temperatures could be observed.

1. Introduction

Over the last few decades tremendous advances have been made in the development of digital electronic devices, which are widely used in human life. The central element of these devices is the processing unit, which in turn consists of millions of transistors. For these devices the trend towards miniaturization remains unbroken. However, the technological evolution has reached a limit regarding the scaling of SiO_2 in metal-oxide semiconductor field-effect transistors (MOSFETs). Below a certain thickness, SiO_2 is no longer an effective gate insulator [1]. This problem can be overcome by replacing SiO_2 with a "high-κ" gate dielectric, which has a higher dielectric constant. Besides HfO_2, rare-earth scandates are among the promising candidates for this application [2–7].

These compounds with the general formula $REScO_3$ where reported as congruently melting for the larger RE^{3+} from La^{3+} (octahedral radius 117.2 pm) down to Dy^{3+} (105.2 pm). All $REScO_3$ within this series crystallize as distorted perovskites in an orthorhombic structure (space group *Pnma*) with pseudocubic lattice constants around 4 Å [8–10]. This makes them also interesting as substrate materials for the epitaxy of other perovskites that are e.g. superconducting, ferroelectric, or multiferroic [11].

Mateika et al. [12] proposed several other substrate materials which are mixed crystals; among them the cubic perovskite $La_{0.29}Sr_{0.71}Al_{0.65}Ta_{0.35}O_3$ (LSAT) became most relevant and is offered commercially meanwhile. Different groups are growing this material with slightly different chemical composition, and with consequently somewhat different lattice constant. Nowadays, LSAT is also considered as prospective substrate material for the epitaxial deposition of GaN layers [13,14].

Besides the somewhat "exotic" $RESCO_3$ and LSAT crystals, sapphire wafers (better to say corundum, α-Al_2O_3) are now the technological basis for the production of nitride light emitting diodes that are used for solid state lighting [15]. Moreover, sapphire crystals are used in scales of tons for windows and watch displays.

During the corresponding crystal growth processes for the production of these materials a sufficient amount of heat must be flowing from the hot melt through the growth interface to the colder seed. The adjustment of these heat flows is not always straightforward. Especially for materials with low optical transmissivity in the near infrared, in combination with low thermal conductivity λ, growth instabilities or even growth disruption can occur. For some $RESCO_3$ the formation of "growth spirals" is a typical problem [16].

* Corresponding author. Leibniz-Institut für Kristallzüchtung, Max-Born-Str. 2, 12489 Berlin, Germany.
E-mail address: detlef.klimm@ikz-berlin.de (D. Klimm).

https://doi.org/10.1016/j.jallcom.2017.12.172
0925-8388/

Another issue is connected with the operation of nanoscale semiconductor devices. There an increased heat generation occurs due to a significant reduction of the dynamic power, whereas the power dissipation per unit area remains constant [17]. Therefore, the heat dissipation characteristics of these devices are of great importance and need to be studied in detail. In this context thermal conductivity is a relevant variable, in order to analyze and model the self-heating behavior of MOSFETs and adjust the device architecture [17–19].

The current study investigates the thermal conductivity of three different rare-earth scandates $DyScO_3$, $TbScO_3$ and $GdScO_3$ in comparison with two widely used compounds $La_{0.29}Sr_{0.71}Al_{0.65}Ta_{0.35}O_3$ (LSAT) and Al_2O_3 (corundum, sapphire). The consideration of sapphire seemed useful because λ data given by several crystal producers are significantly different: For the [100] and [001] directions one finds e.g. 23.0 and 25.8 W/(m·K) at room temperature [20], whereas another reference reports 42 W/(m·K) without specification of the crystallographic direction [21]. Other references report a larger conductivity in [100] than in [001] [22]. Data for elevated temperatures are extremely scarce (but see Ref. [21]). This paper will report and compare experimental data for the crystals mentioned above. All single crystals were grown in the author's laboratory under similar experimental conditions, and also the $\lambda(T)$ measurements were obtained under identical conditions for all samples.

2. Theoretical background

When a temperature gradient is applied to a solid object, thermal energy will flow from the warmer to the cooler zone. The thermal conductivity $\vec{\lambda}$ is a material property, which describes the rate of heat transport in the object relating the local heat flux $\vec{J}$ to the temperature gradient $\partial T/\partial x \equiv \vec{\nabla} T$ [23,24].

$$\vec{J} = -\vec{\lambda} \cdot \vec{\nabla} T \tag{1}$$

Like for other transport properties, $\vec{\lambda}$ is a symmetric second rank tensor, which defines the relation between an applied and resultant vector. Thus, for an anisotropic material it consists of a maximum of six independent components. Though this number can be reduced by consideration of the crystal symmetry [24]. For the different crystal systems one obtains the following numbers of independent components that are given in brackets: triclinic (6); monoclinic (4); orthorhombic (3); trigonal, tetragonal, hexagonal (2); cubic (1) [25]. This means that only in cubic, polycrystalline or other isotrope materials the thermal conductivity is described by one number λ.

All rare-earth scandates are orthorhombic perovskites [26]. Sapphire (α-Al_2O_3) has a trigonal structure [27] and LSAT is cubic [28]. This means that only three or less components of thermal conductivity need to be measured in order to describe the corresponding $\vec{\lambda}$ tensors.

The thermal conductivity of a given material can be derived from the thermal diffusivity a, because these two properties are linked by

$$\lambda = \varrho \cdot c_p \cdot a \tag{2}$$

where c_p is the specific heat capacity and ϱ the mass density [29].

Equation (1) describes only the heat that is transported through the solid via phonons, electrons, or any other carriers. In transparent media, an additional share of heat energy is transported by radiation. Fortunately, both mechanisms work on very different time scales, because heat radiation moves with the speed of light; phonons in contrast move with the speed of sound. In the laboratory scale for distances around 1 mm this means that heat radiation arrives almost immediately, whereas conducted heat (1) arrives after ca. 1 ms, which can be separated well [30].

3. Experimental

The crystals investigated in this study were grown by the conventional Czochralski technique from a cylindrical iridium crucible and in a growth atmosphere of flowing argon. For the growth of LSAT, typically 10% CO_2 were added to Ar. The pulling rates were typically 1.0–1.5 mm/h and the rotation rates between 8 and 15 rpm [14,31,32]. The thermal conductivity as a function of temperature was determined according to equation (2). For this purpose, temperature dependent measurements of thermal transport and heat capacity were performed on the samples, while the mass density ϱ was taken from the literature [9,10,32–36]. Table 1 lists the data used for ϱ near room temperature. The average linear expansion coefficient $\overline{\alpha}$ was used to calculate the temperature dependence of the density and the thickness by the change of the sample dimensions. It should be mentioned, however, that the relative change of thickness upon heating by $\Delta T \approx 1000$ K is only $\overline{\alpha} \cdot \Delta T$, which is in the order of 1%. Correspondingly the influence on ϱ is in the order of $3 \cdot \overline{\alpha} \cdot \Delta T$, which is 3%.

The specific heat capacity c_p was measured by heat flux differential scanning calorimetry (DSC) with a NETZSCH STA449C. For this purpose, three DSC measurements with linear heating ramps were performed: first with an empty crucible as baseline correction, second with a reference substance where $c_p(T)$ is known and third with the sample to analyze [37]. The heat capacity was then calculated by comparison of the obtained curves using the DIN 51007 method.

All DSC measurements were carried out in Pt crucibles with lids in flowing argon. The crystal samples were pestled to crush and Al_2O_3 powder was used as reference. To ensure reproducibility, four subsequent heating runs with 20 K/min from 313 K to 1473 K were performed during every measurement. Because the first run showed higher experimental scatter and deviated by up to 15% from the following runs, solely the average values of the subsequent runs were used to determine $c_p(T)$.

The thermal diffusivity a was measured by laser flash technique with a NETZSCH LFA427. To determine $a(T)$ with this method the bottom side of the sample was irradiated by a Nd:YAG laser, which generated a heat pulse. Transport of that heat thought the material resulted in a rise of the temperature on the top of the sample, which was measured and evaluated [29]. For this purpose, the temperature time response was fitted by Mehlings model [30] for semi-transparent media to obtain $a(T)$.

LFA measurements were performed on sample slices with thicknesses of approximately 1.5 mm and diameters between 6 and 12 mm, which were cut to give slice orientations (100), (010) or (001), respectively. To ensure uniform heat absorption, the samples where covered with a thin layer of graphite prior to every

Table 1
Mass density at room temperature ϱ and average linear expansion coefficient $\overline{\alpha}$ of the investigated compounds.

Crystal	ϱ (g/cm^3)	$\overline{\alpha}$ (10^{-6} K^{-1})
$DyScO_3$	6.90 [9]	8.4 [32]
$TbScO_3$	6.55 [10]	8.2 [32]
$GdScO_3$	6.66 [9]	10.9 [32]
LSAT	6.65 [34]	9.9 [33]
sapphire	3.99 [36]	7.7 [35]