Diffusion Characteristics of Cr Dopant in Cr:ZnS Crystals via Laser Ablation–Inductively Coupled Plasma Mass Spectrometry Analysis

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INTRODUCTION

Mid-infrared lasers emit over a wavelength range of 2–5 μm , which overlaps with the characteristic absorptions of various organic and inorganic molecules; hence, such lasers have been widely applied in free-space communication, remote sensing, and medical diagnostics (1–3). Chromium-doped zinc sulfide (Cr:ZnS), first reported in detail by Page and Deloach et al. in 1996 (4), is one of the most important materials for use in mid-infrared laser gain media. As a transition-metal-ion-doped II–VI compound, Cr:ZnS exhibits high quantum efficiency at room temperature, large absorption and emission cross-sections, and low excited-state absorption (5–7). To prepare Cr:ZnS crystals, Cr ions can be introduced into the chalcogenide host by multiple methods, including modified vertical Bridgman crystal growth, post-growth diffusion, and physical vapor transport; the simplest and most cost-effective methods are those based on diffusion (8). However, doping during the diffusion process often results in spatially variable dopant concentrations which is detrimental to laser performance, especially in terms of laser beam stability. Thus, it is imperative to know the diffusion characteristics for crystal growth.

Cr²⁺ species are responsible for imparting the desirable properties of Cr:ZnS crystals, although two

ABSTRACT

Laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) was applied to characterize the diffusion behavior of doped Cr ions in ZnS crystals, in terms of Cr concentration, diffusion distribution, and diffusion coefficient. For quantification, calibration was performed with matrix-matched specimens prepared by diffusion techniques. The distributions of Cr at the crystal growth cross-sections were determined by quantitative mapping to estimate the ion diffusion paths. Spatial variance of the Cr ions was obtained, revealing a sharp doping concentration gradient in the ZnS crystals. Based on the Cr distance-concentration data measured by LA-ICP-MS, the diffusion coefficients for Cr in the ZnS crystals were calculated using Fick's Second Law (simplified). The coefficient values increased with increasing temperature. This study provides not only a practical approach to the measurement of the distribution of a low-level dopant in crystals, but also a computational method for calculating diffusion coefficients from LA-ICP-MS data.

additional charge states (Cr¹⁺ and Cr³⁺) may possibly be present. Previous studies have demonstrated that Cr²⁺ accounts for greater than 90% of all Cr species (9–11). Hence, the total Cr concentration can be considered instead of the Cr²⁺ concentration. Typically, ultraviolet–visible–near-infrared (UV-Vis-NIR) spectrophotometry and inductively coupled plasma atomic emission spectrometry (ICP-AES)

are used to analyze the Cr²⁺/Cr content in Cr:ZnS crystals. The accuracy of these two methods is related to the uniformity of the element distributions. In addition, for ICP-AES analysis, the samples must be pulverized and prepared as solutions, which can be inefficient and time-consuming. Electron probe microanalysis (EPMA) is a reliable technique for the study of inner diffusion processes (12–14). However, owing to its moderate sensitivity, the ability to detect elements at low concentrations is limited for EPMA.

Laser ablation–inductively coupled plasma mass spectrometry (LA-ICP-MS), which combines the advantages of the high sensitivity and low detection limits of MS and the high spatial resolution of lasers, is an attractive analytical technique for the direct analysis of solid samples. It has been used for the determination of major and trace elements and the measurement of isotope ratios, as well as in microanalyses, in-depth profiling, and surface mapping (15). With the increasing need to characterize complex solid specimens, LA-ICP-MS has been widely employed in many fields, including geology (16, 17), biology (18, 19), and the environmental (20, 21) and material sciences (22, 23). However, few synthetic crystals have been studied via LA-ICP-MS. Elemental analyses of single SiC crystals (24), ZnS_{1-x}Se_x crystals (25), La₃Ga_(5.5+x)Si_(0.5-x)O₁₄ crystals (26), and PbF₂ crystals (27) have been reported. These studies focused mainly on the analysis of the concentration and distribution of impurities or the major components of the crystals. However, few

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reports have described the doping behavior of the elements in crystals as determined by LA-ICP-MS.

In this work, LA-ICP-MS was employed to investigate the diffusion behavior of Cr in Cr:ZnS crystals, including the elemental concentration, distribution, and diffusion coefficient. Quantitative distribution images for the Cr dopants in the Cr:ZnS crystals were obtained via data calibration by matrix-matched specimens prepared by a post-growth diffusion method. To estimate their feasibility as calibrants, the contents and homogeneity of these specimens were analyzed by ICP-AES and LA-ICP-MS. The spatial variance of the Cr ions in the ZnS crystals was obtained by the mapping of Cr at the crystal growth cross-sections, revealing a sharp concentration gradient in the crystal. The results were validated by the synchrotron X-ray fluorescence (SXRF) method. Based on the Cr distance-concentration data measured by LA-ICP-MS, diffusion coefficients were calculated using a simplified Fick's Second Law model. For the three crystals separately prepared at 750, 850, and 950 °C, the diffusion coefficient values tended to increase significantly with temperatures.

EXPERIMENTAL

Instrumentation

A quadrupole-based X Series II ICP-MS system (Thermo Fisher, USA), combined with an LSX-213 laser ablation system (CETAC Technologies, USA), was used for Cr:ZnS crystal analysis. Table I summarizes the typical experimental parameters. Helium, used as the carrier gas for cell purging, was mixed with argon when introduced into the plasma. The helium flow rate during measurement was 0.6 L min⁻¹. The samples were ablated with line- and surface-scan patterns. A delay time of 10 seconds was applied before laser firing. The diameter of

the laser beam was 100 μm and the scan rate was 100 μm s⁻¹. The ⁵²Cr isotope was chosen for detection. SXRF microprobe experiments were performed at the beamline BLU151, Shanghai Synchrotron Radiation Facility. Incident X-rays of 8 keV were employed to excite the Cr in the crystals. The SXRF signals were collected at a spot size of 150 μm and a step size of 300 μm. The bulk concentration of Cr was determined by ICP-AES (Varian Vista AX, USA). Doubly deionized water (DIW, 18.25 MΩ·cm) was obtained from a Milli-Q[®] water system (Millipore Corporation, USA).

Reagents and Materials

High-quality 65% HNO₃ (GR, Sigma-Aldrich, Germany) and 37% HCl (MOS, FengChuan, P.R. China) were used to dissolve the Cr:ZnS crystals. The solutions were prepared with DIW. The element standards were diluted from 1000 mg/L Cr aqueous standards (NCS, P.R. China). All Cr:ZnS crystal samples, including the matrix-matched specimens, were obtained from the Key Laboratory of Transparent Opto-

TABLE I
Main Operational Parameters
for LA-ICP-MS

ICP-MS Operational Parameters	Value
RF power	1300 W
Sampling depth	7.5 mm
Sampling gas flow	0.72 L min ⁻¹
Auxiliary gas flow	0.80 L min ⁻¹
Coolant gas flow	13 L min ⁻¹
Signal acquisition mode	TRA
LA Operational Parameters	Value
Laser wavelength	213 nm
Laser energy	40%
Ablation spot size	100 μm
Laser frequency	20 Hz
Scan rate	100 μm s ⁻¹
Testing isotope	⁵² Cr

functional Inorganic Materials of the Shanghai Institute of Ceramics at the Chinese Academy of Science.

Preparation of Samples and Matrix-matched Standards

A typical post-growth diffusion method was applied to prepare the high-quality Cr:ZnS crystals (10). In brief, polycrystalline ZnS was grown by chemical vapor deposition. A Cr film was deposited on the ZnS surface by the filtered arc deposition (FAD) method. The samples were then sealed in vacuum silica tubes and diffused at high temperature (750, 850, or 950 °C). The residual surface Cr film was removed by polishing before LA-ICP-MS detection. To obtain uniform specimens that could be used as calibrants, the thick ZnS pieces (~0.5 mm) were subjected to diffusion at 950 °C for more than two weeks by the same diffusion method.

Acid Digestion of Cr:ZnS Crystals for ICP-AES Analysis

The crystals were washed with DIW and dried completely before being pulverized. Each sample (0.15 g) was accurately weighed into a PTFE vessel and heated with *aqua regia* (3 mL) until completely dissolved. The solution was allowed to cool before transfer to a 100 mL volumetric flask and dilution to 100 mL with DIW. The final solutions were analyzed by ICP-AES.

Calculation

The diffusion coefficient of a material is a physical constant which indicates its ability to undergo diffusion. This parameter is particularly important in crystals grown by diffusion methods. For diffusion doping, the accumulation of the dopant ion at a certain point can be expressed by the vector notation of Fick's Second Law. As for the case in this study, the equation is simplified to a one-dimen-

sional semi-infinite model as follows:

Eq. (1)

$$c(x, t) = \alpha / \sqrt{\pi D t} \exp(-x^2 / 4 D t)$$

Here, D is the diffusion coefficient at a certain temperature; $c(x, t)$ is the concentration of Cr at a distance x from the surface after diffusion for a time t ; and α is the amount of Cr per unit area at the surface. From this function, if we know the concentrations at specific locations, D can be calculated.

The activation energy (Q) and pre-exponential factor (D_0) were calculated based on the diffusion coefficients and temperatures. According to the Arrhenius relationship, the calculated diffusion coefficients could be plotted in terms of $\log D$ versus $1/T$, from which Q and D_0 were calculated as follows:

Eq. (2)

$$D = D_0 \exp(-Q/RT)$$

To guarantee the validity of the semi-infinite model, three measurements were taken in our experiments. (a) The quantity of dopant source was more than the host could accommodate during the diffusion process. (b) The host thickness was longer than the diffusion length of Cr ions to avoid the overlap of dopant ions from both sides. (c) To minimize the influence of small lateral diffusion, the laser ablation path was settled in the middle of the cross-section.

RESULTS AND DISCUSSION

Homogeneity of the Matrix-matched Standards and Calibration Curve

Elemental fractionation and the lack of reference materials for a sample of interest often restrict quantitative analysis (15). For the Cr:ZnS crystals, there are no appropriate commercial references for quantification, which prompted the

in-house preparation of matrix-matched standards. Although uniform distributions in standards are required, it is difficult and time-consuming to achieve homogeneity by diffusion methods. Several factors such as the diffusion time, temperature, and diffusion depth were investigated, with the optimized conditions as described in the "Preparation of Samples and Matrix-matched Standards" section. To verify homogeneity, LA-ICP-MS in the line-scan mode was applied. Three random sites were ablated under the same experimental conditions. Figure 1 shows the MS signal intensities of the ZnS blank and two Cr:ZnS standards with different Cr concentrations. The flat, stable signals that were obtained imply the uniform distribution of Cr in the

crystals. The bulk Cr concentrations in the two standards are 0.027% and 0.058%, as analyzed by ICP-AES. A plot of the MS signals and concentrations exhibits excellent linearity (Figure 2) with a linear correlation coefficient (R^2) of 0.999. Thus, these in-house-prepared standards are appropriate for calibrating the analysis results for quantification.

Quantification and Distribution Imaging of Cr in Cr:ZnS Crystals

Important information along the diffusion path can be elucidated for crystals grown by the diffusion method, including the doping concentration and element distribution. To evaluate the diffusion behavior of Cr in the Cr:ZnS crystals, the

Fig. 1. LA-ICP-MS signal intensity of ^{52}Cr at three separate locations in the Blank, Standard-1, and Standard-2 samples.

Fig. 2. Correlation between Cr signal intensities and concentrations in the standards.

crystals were cut in half cross-wise, and one-half of each cross-section was selected as the target area (as indicated in Figure 3 e and f). Two Cr:ZnS crystals (Sample-1 and Sample-2) were measured. The images in Figure 3 show the Cr:ZnS crystals after diffusional growth. Samples were adhered to the ablation cell using double-sided tape to keep the axial sections horizontal, and the surface-scanning mode was applied. The results were calculated against the in-house matrix-matched standards.

Quantitative maps of Cr in the cross-sections were obtained (Figure 4) from the images, the diffusion of Cr can be visually observed. Sharp concentration gradients are clearly evident in both samples. Although they have different Cr concentrations and distributions, the diffusion paths are similar. In general, high levels of Cr ions are situated near the surface, with reduced concentrations toward the

middle. This phenomenon may be caused by ion motion in the materials: during diffusion, the doped ions transfer from the higher to the lower concentration regions until a dynamic balance is attained. However, the small degree of freedom in solid materials and the low diffusion coefficient limit this transportation, thereby easily resulting in a gradient distribution. Thus, because of such gradients, the concentration near the surface is higher than that internally. Moreover, if Cr powder is deposited on the side surface of the crystals during preparation, the overlap of Cr ion diffused from more than one direction and results in particularly high concentrations, as shown in the top left corners. The LA-ICP-MS results were validated by the SXRF method (Figure 5). The resulting fluorescence intensity distribution images are in good accordance with the results obtained by LA-ICP-MS.

Diffusion Coefficients

Three Cr:ZnS crystals prepared at different diffusion temperatures (750, 850, and 950 °C) were evaluated (Figure 6). The diffusion curve was smoother and the diffusion distance was longer at 950 °C than at 850 and 750 °C, implying that higher temperature promotes the transportation of ions in the crystals. Curves were fit and the coefficients of determination (R^2) were obtained to compare experimental and theoretical results. All measured curves were in good agreement with the diffusion model ($R^2 > 0.9$). The values of D in the crystals at 750, 850, and 950 °C calculated by Eq. (1) are 2.89×10^{-10} , 15.1×10^{-10} , and $39.8 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, respectively. Thus, with increasing temperature, the value of D is significantly increased. The calculated diffusion coefficients were plotted in terms of $\log D$ versus $1/T$ (Figure 6). According to Eq. (2), two other important physi-

Fig. 3. Physical appearance of Cr:ZnS crystal samples. (a), (c), and (e) are Sample-1; (b), (d), and (f) are Sample-2. (a) and (b): before polishing; (c) and (d): after polishing; (e) and (f): axial section cut-off along the diameter.

Fig. 4. Quantitative imaging (concentration distribution) of Cr in Sample-1 (left) and Sample-2 (right) by LA-ICP-MS.

TABLE II
Parameters for Cr Diffusion in ZnS Crystals

Sample	D (cm ² s ⁻¹ , 10 ⁻¹⁰)			Q (kJ mol ⁻¹)	D ₀ (cm ² s ⁻¹ , 10 ⁻⁴)
	750 °C	850 °C	950 °C		
Cr:ZnS	2.89	15.1	39.8	137.1	30.9

Fig. 5. Distribution imaging of Cr (signal intensity) in Sample-1 (left) and Sample-2 (right) by SXRF.

cal parameters – the activation energy (Q) and pre-exponential factor (D₀) – were calculated. Table II summarizes the D, Q, and D₀ results. For Cr:ZnS, the relatively low D and high Q values demonstrate the difficulty of Cr diffusion in the ZnS crystals.

CONCLUSION

In this study, the diffusion behaviors of Cr ions in Cr:ZnS crystals, including the diffusion path (concentration and distribution) and diffusion coefficient, were investigated by LA-ICP-MS for the first time. Axial sections of the prepared crystals were analyzed to evaluate the diffusion process. From quantitative imaging, spatial variances for the Cr ions in the ZnS crystals were clearly observed. There were sharp gradient distributions from the outside to the inside. Using the distance-concentration relationship measured by LA-ICP-MS,

Fig. 6. Measured and fitted curves of Cr at different temperatures of 750, 850, and 950 °C (left), and the relationship between D and T (right) in ZnS crystals prepared for one day.

the diffusion coefficients and activation energy were calculated. The diffusion coefficients for Cr in the ZnS crystals prepared at 750, 850, and 950 °C were 2.89×10^{-10} , 15.1×10^{-10} , and 39.8×10^{-10} cm² s⁻¹, respectively, and the activation energy (137.1 kJ mol⁻¹) was high. These distribution data and diffusion parameters could help to elucidate the mechanism for doping elements into crystals and the progress of diffusion. This approach also demonstrates the potential for optimizing new crystal-growing processes, which could yield high-quality samples.

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