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Production yield of rare-earth ions implanted into an optical crystal

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Rare-earth (RE) ions doped into desired locations of optical crystals might enable a range of novel integrated photonic devices for quantum applications. With this aim, we have investigated the production yield of cerium and praseodymium by means of ion implantation. As a measure, the collected fluorescence intensity from both implanted samples and single centers was used. With a tailored annealing procedure for cerium, a yield up to 53% was estimated. Praseodymium yield amounts up to 91%. Such high implantation yield indicates a feasibility of creation of nanopatterned rare-earth doping and suggests strong potential of RE species for on-chip photonic devices. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4941403>]

Crystals doped with rare-earth (RE) ions, well known due to their key application in laser technology, additionally aspire to become a viable contender in solid-state quantum information processing. With landmark achievements like coherent manipulation¹ and all-optical addressing of a single ion spin,² up to 6 h long storage times of quantum states,³ and quantum memory for entangled photon pairs,⁴ RE doped crystals show strong potential in quantum optics research and technology.

Typically, crystals are doped during their growth to generate optically detectable RE ensembles.⁵ Scalable, integrated quantum networks, however, require nanoscopic engineering of RE ions, in order to employ them as stationary qubits. Ion implantation as a means for controlled doping of crystals is, therefore, a prerequisite for a more versatile implementation in experiments, as was the case for nitrogen vacancy (NV) centers in diamond.^{6–10} However, as known from the studies of implantation yield of NV centers, not every implanted ion becomes necessarily fluorescent.¹¹ Thus, assessment of the fraction of the implanted ions that become fluorescent is required.

In this letter, we report on the creation efficiency of trivalent cerium and praseodymium ions in yttrium aluminum garnet (YAG) doped by ion implantation. A wide range of ion fluences and implantation energies was used in order to obtain a comprehensive picture of the production yield of two promising RE ion species in YAG. Also, post-implantation annealing atmospheres were investigated, and an advantageous approach for yield estimation is presented. The motivation behind these experiments is to optimize the generation of fluorescent RE ions in crystals by means of ion implantation.^{11–13}

Trivalent RE ions can easily substitute yttrium ions in the crystal lattice of YAG, thus forming color centers

featuring optical transitions with high quality factor. Foundation of these high-Q transitions are electrons located in the partially filled 4f shell of RE ions, which are shielded from the environment by closed outer 5s and 5p shells. This results in long coherence times of both electron spin and nuclear spin. In the experiment, cerium and praseodymium ions are used as dopants, and their fluorescence intensity is detected in home-built high resolution confocal and upconverting microscope setups, respectively.

Trivalent praseodymium ions in YAG are excited by a two-step upconversion process,¹⁴ with a diode laser of 488.25 nm wavelength. The first excitation step involves a spectrally narrow, parity forbidden 4f-4f transition from ³H₄ ground state to ³P₀ state, as depicted in Fig. 1(a).¹⁵ In ³P₀, the electron exhibits a lifetime of 8 μs, during which it is able to absorb another photon and thus is promoted into the 4f5d(2) band, where non-radiative decay onto the lowest 4f5d(1) level occurs. The 4f5d shell enables parity-allowed optical transitions with a lifetime of approximately 18 ns to 4f states, featuring ultraviolet fluorescence detected in a

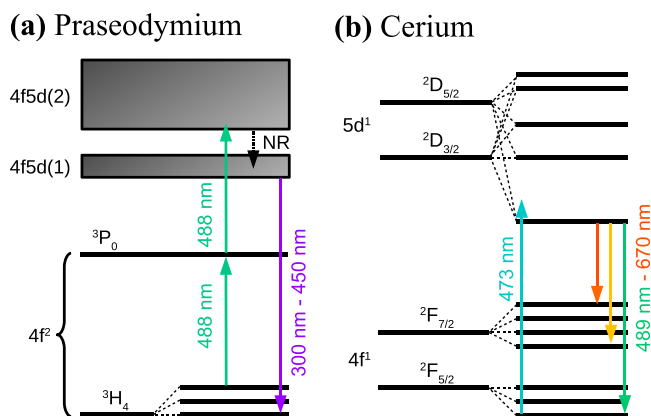


FIG. 1. Electronic level structures of (a) praseodymium and (b) cerium with employed excitation and emission wavelengths. NR: non-radiative decay.

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spectral range of 290–370 nm.¹⁶ Due to the high cycling rate, this scheme previously allowed detection of single Pr^{3+} centers in YAG.¹⁷

As shown in Fig. 1(b), trivalent cerium ions in YAG are non-resonantly excited with a diode laser of 473 nm wavelength, thus pumping the $4f^1$ ground level to the lowest $5d^1$ level, which exhibits a lifetime of 60 ns.¹⁸ Its strong phonon-sideband emission is related to the $5d-4f$ transition, which is detected in a 491–630 nm spectral window. Quantum efficiencies of these transitions are close to unity.¹⁹ Single ion detection of both cerium and praseodymium plays a key role in fluorescence yield estimation.^{17,20}

To obtain a robust yield estimation, the following sample processing was carried out. Before implantation, samples are covered with a perforated copper mask. For that, monodisperse SiO_2 (nanospheres radius $r_{\text{sphere}} \approx 210$ nm) are spin-coated onto the polished surface of the crystal. The nanospheres were prepared by a sol-gel method as described in the supplementary material.²¹ A subsequent copper evaporation step results in a 200 nm thick copper layer. Then, the SiO_2 spheres are removed, leaving uniform holes in the copper mask, as illustrated in Figure 2(a). RE ions were subsequently implanted through the mask, as depicted in Figure 2(b). After implantation, the copper mask is removed from the crystal by wet etching in FeCl_3 solution. Samples are then annealed in different atmospheres at 1200 °C for 24 h. The annealing serves three purposes: (1) the crystalline structure damaged by implantation is restored; (2) the implanted ions replace yttrium ions in their sites; and (3) the implanted ions get

stabilized in an optically active trivalent state. Praseodymium-implanted samples are annealed in air. For cerium, previously conducted studies suggest a reducing atmosphere^{22–24} to improve stabilization in the desired charge state in the crystal. Our preliminary experiments confirmed this behavior in a reducing atmosphere of argon and hydrogen (95%/5%) when compared with an inert argon atmosphere. In previous work,² we reported gradual bleaching of Ce^{3+} centers under continuous wave (CW) excitation, while they are photostable under femtosecond illumination. On the contrary, cerium ions in the samples annealed under $\text{Ar} + \text{H}_2$ atmosphere are photostable under CW excitation and, therefore, allowed us to use CW diode laser for the optical studies.

We used an EIKO E-100 focused ion beam (FIB) system for implantation, where ions are extracted from a homemade liquid metal ion source (LMIS),²⁵ containing an alloy of either cerium $\text{Au}_{78.4}\text{Si}_{11.6}\text{Ce}_{10}$ (at. %) or praseodymium $\text{Au}_{78.4}\text{Si}_{11.6}\text{Pr}_{10}$ (at. %). The implantation energy ranged between 75 keV and 300 keV and determined the expected depths of implanted ions. Figure 2(c) shows Stopping and Range of Ions in Matter (SRIM) simulations²⁶ regarding ion depths, together with the longitudinal straggle depending on the implantation energy. The FIB was scanned across the sample surface in the fashion of an area implantation to ensure homogeneous implantation fluence, as shown in Fig. 2(d).²⁷ Detailed description of area implantation with an FIB and the corresponding fluence calculation are covered in the supplementary material.²¹

Ion fluence ranged between 10^{12} ions/cm² and 10^{14} ions/cm². This results in a dynamic range of up to five orders of magnitude, as single ion fluorescence needs to be compared with up to $\sim 130\,000$ fluorescing ions in one spot. In order to overcome the limitations imposed by the fluorescence detector and to avoid center saturation, the laser needs to be operated in the linear excitation power range of the respective ion species and the linear intensity range for the detector. Therefore, power studies were carried out. For cerium, a two-level rate equation model was used to fit the measured data, as shown in Figure 3(a). Solution to the two-level approach is the laser power dependent single center fluorescence intensity

$$F_{\text{sc}}(I) = A \frac{I}{I + I_0}, \quad (1)$$

where A is the maximum fluorescence intensity of a single ion and I_0 is the saturating laser power.

Due to the two-step upconversion in the case of praseodymium, ion saturation is far less likely, so that only detector saturation was monitored in the power study, shown in the supplementary material.²¹

For production yield estimation of implanted RE ions, we modeled the emission of implanted spots and compared it with the measured emission. Modeling of the spot emission is based on the single RE ion point spread function (PSF). The inset in Figure 3(b) displays the corresponding 2-D laser scanning microscope image of a single cerium ion. By fitting a Gaussian function to a cross section scan of a single RE ion, we obtain the PSF radius, shown in Figure 3(b). For each of the two microscopes used for single RE ion

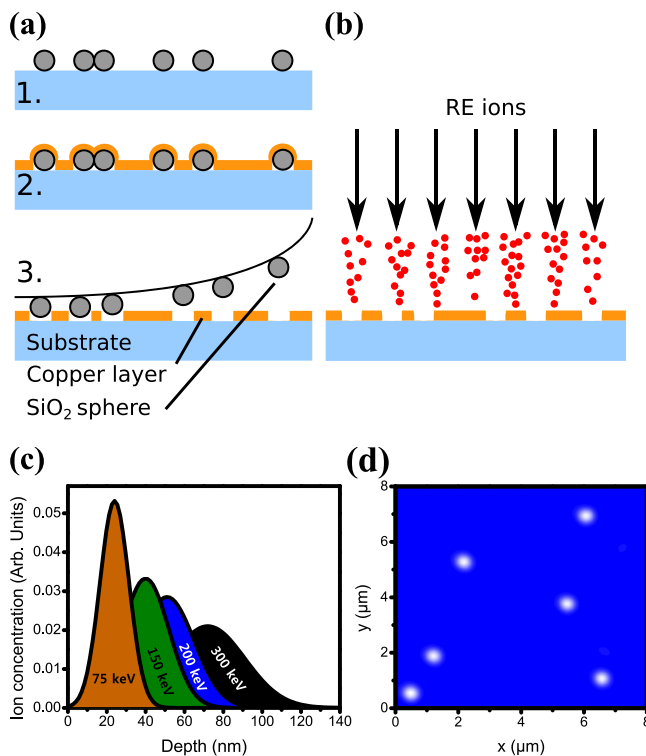


FIG. 2. (a) Mask-making process is illustrated in three steps. (b) Area implantation through mask. (c) Simulated implantation depths of cerium ions implanted into YAG in dependence on four different implantation energies. (d) Exemplary confocal image of the surface of an implanted sample. Individual bright spots implanted through the holes in the mask show the same brightness, indicating homogeneous implantation fluence.

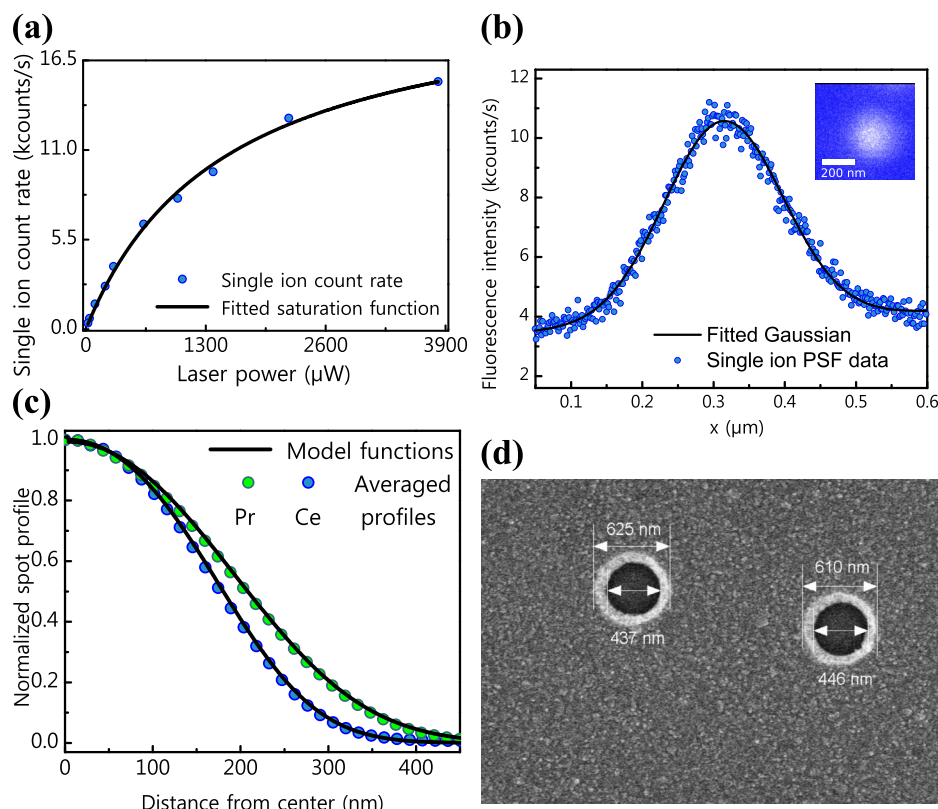


FIG. 3. (a) Cerium power study on a single center. The corresponding fit yields a saturation laser power of $I_0 = 1500 \mu\text{W}$. Accordingly, fluorescent measurements were taken at $300 \mu\text{W}$, well below this threshold to avoid saturation effects. (b) Measured PSF of a single cerium ion and corresponding Gaussian fit. Inset: 2-D laser scanning microscope image of a single fluorescent cerium ion. Scale bar: 200 nm. (c) Averaged spot profiles with corresponding spot model fits. (d) SEM image of the copper mask.

detection, we obtained a different PSF. The emission profile of the implanted spot is given by the convolution of the PSF of the microscope with the distribution of the implanted ions

$$F_0(\mathbf{r}') = \int \mathbf{r} \varrho(\mathbf{r}) I_{\text{PSF}}(\mathbf{r} - \mathbf{r}') d\mathbf{r}, \quad (2)$$

where $\varrho(\mathbf{r})$ is the spatial distribution of the implanted ions and $I_{\text{PSF}}(\mathbf{r})$ is the characteristic emission of a single ion. More detailed description of modeling $\varrho(\mathbf{r})$ is given in the supplementary material.²¹ Spot emission profiles were extracted from fluorescent scans of implanted spots, averaged and fitted with $F_0(\mathbf{r}')$ as depicted in Figure 3(c). Due to different microscope PSF, spot emission profiles for the two RE ion species vary slightly. Furthermore, a copper mask characterization was done with SEM, where holes were found to also feature a rim, as depicted in Figure 3(d). However, implanted RE ions can only penetrate through the inner part of the rim, where the copper layer is thinner than the energy-dependent penetration depth of RE ions into copper. For energies of 75 – 300 keV, the penetration depth ranges between 15 and 45 nm according to SRIM simulations. Consequently, rim widths obtained directly through SEM measurements decrease to the effective rim width r_{rim} . Holes were found to have a radius $r_{\text{hole, SEM}} = 221 \pm 3$ nm, with a rim of an effective width $r_{\text{rim, SEM}} = 15 \pm 5$ nm. For comparison, spot profiles obtained from optical measurements of both praseodymium-implanted and cerium-implanted samples were fitted with the introduced model. As a result, the modeled hole radius amounts to $r_{\text{hole, fit}} = 206 \pm 19$ nm and the modeled rim width amounts to $r_{\text{rim, fit}} = 5 \pm 5$ nm. Our approach can confirm the copper mask parameters measured by SEM.

Figures 4(a) and 4(b) show the efficiency of the produced RE ions in their fluorescing RE^{3+} charge state for different implantation energies as a function of the ion fluence.

At least ten implanted spots were measured for each plotted data point in these figures. The figures show a decrease in yield with increasing fluence of implanted ions. Higher implantation energies feature a higher yield. For higher energies, ions exhibit a larger straggle, longer travel distance in the crystal, and they also generate more defects per implanted ion. All these effects can contribute to a higher possibility for implanted RE ions to settle in the crystal lattice and to be activated after annealing.

The fluence-dependent behavior may be explained by an increase in local RE ion density with increasing ion fluence. As the straggle volume for each ion energy stays constant for a varying fluence, the final amount of RE ions within the same volume is fluence-dependent. The more ions are implanted in such a space, the less likely it is for the individual ion to find a proper location to replace yttrium. Peak production yield values are 91% for praseodymium and 53% for cerium for the lowest ion fluence in each case. In principle, both values can reach unity, provided ideal activation procedures are found.

In conclusion, this quantitative study confirms high production yield values for implanted RE ions. Reported values of other color centers, such as silicon vacancy centers in diamond, show a yield of 15% with an implantation energy of 60 keV.²⁸ Investigation into nitrogen vacancy center generation in diamond meanwhile reached production yield values of 25% for implantation energies between 2.5 keV and 20 keV (Ref. 29) and almost 50% for implantations at MeV energies.¹¹ Unreached is the activation rate of praseodymium, with almost unity yield. This suggests that single ion implantation is feasible.³⁰ In turn, high spectral stability of the optical lines of the implanted RE^{3+} ions reported in our previous work² makes them very favorable candidates for

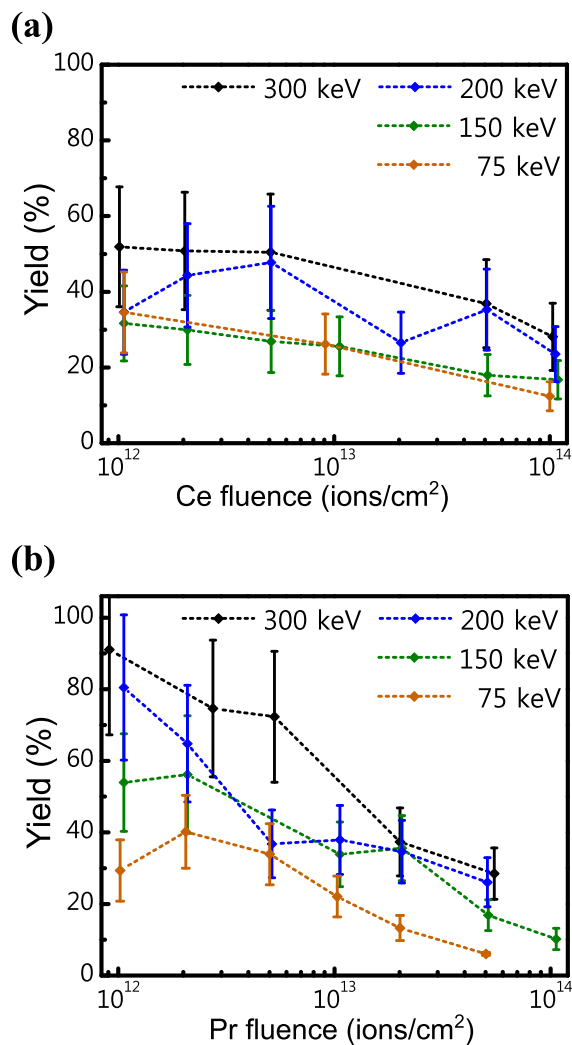


FIG. 4. Production yield of implanted (a) cerium ions and (b) praseodymium ions for four different implantation energies.

optically addressable single ion qubits. This work also paves the way toward low energy implantations in the range of 0.1 – 10 keV, which would result in deterministic high resolution nano-positioning of RE ions. Under which conditions a high production yield for RE ions can be maintained for such low energy implantations has yet to be investigated.

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