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Creation and physical aspects of luminescent patterns using helium ion microscopy

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The helium ion microscope provides a sub-nanometer size He⁺ ion beam which can be employed for materials modification. We demonstrate how material properties can be tuned in a helium ion microscope with very high precision using, as an example, the modification of the luminescence properties of a sodium chloride crystal. Although the beam size is extremely small, the actually affected sample volume is much bigger due to collision cascades. We have directly measured the diameter of the interaction volume of the 35 keV He⁺ beam with a sodium chloride crystal using ionoluminescence. The experimental results are compared to stopping and range of ions in matter simulations and calculations of the point spread function. © 2014 AIP Publishing LLC

I. INTRODUCTION

Local modification of material properties is an interesting topic since it gives an opportunity to tune the material parameters for one’s needs and by doing so, design various devices. In this context, the helium ion microscope (HIM) is an attractive and powerful tool. It provides a He⁺ ion beam with a spot diameter of 0.4 nm.1,2 HIM has been successfully employed for surface patterning and nanofabrication.2–12 Here, we demonstrate how HIM can be applied for precise modification of bulk material properties.

Mainly, secondary electrons (SEs) are used for imaging. We use the term “SE” throughout this paper for those electrons, which are generated as a result of an ion impact, that actually make it to the surface and are emitted into the vacuum. In addition to SEs and backscattered He signals typically used in HIM, also photon generation and detection is possible for certain materials.13–15 This phenomenon is called ionoluminescence (IL). The ion beam is able to not only induce light emission from the sample but can also change the luminescence properties of the material. We employ both aspects for patterning of luminescent structures and direct visualization of the beam-matter interaction volume. Determining the actual size of the interaction volume and understanding the development of the affected area with increasing ion fluence are of importance for HIM applications like resist development, direct lithography, defect engineering, and many more.

Irradiation of alkali halides with ionizing radiation (e.g., electron and ion beams, X-rays) causes defect formation and subsequent crystal coloration.16,17 The influence of a He⁺ ion beam on NaCl in terms of ionoluminescence has been studied previously.13 Light emission under the influence of an ion beam is the result of recombination of the created color-centers (in particular, F- centers) with charge carriers. In NaCl, F- centers are chlorine ion vacancies filled with one electron. They are created both by direct nuclear collisions and via electronic excitations.18,19 Generation of color-centers with an ion beam gives local control over the defect density.

II. EXPERIMENTAL

The experiments were performed in an ultra high vacuum (UHV) Orion Plus helium ion microscope from Carl Zeiss NTS20 at room temperature. In the standard HIM imaging mode, an image is created by collecting SEs with an Everhardt–Thorlency (ET) detector. An IL image can be recorded simultaneously by collecting the emitted photons with a Gatan MonoCL4 Elite system. The system is equipped with a Hamamatsu Photomultiplier tube (PMT) R943-02 utilized for panchromatic IL imaging in the presented work, and a CCD detector PIXIS:100 from Princeton Instruments for parallel spectrum acquisition. Further details on the system configuration can be found in Ref. 13.

The primary energy of the He⁺ ion beam was 35 keV, the beam was oriented perpendicularly to the surface. In the present experiments, the beam current has been varied between 0.5 and 6.6 pA. All images were acquired simultaneously, using the ET and PMT detectors. The chamber pressure of the baked sample chamber was in the low 10⁻⁹ millibar range during all measurements.

Additional cathodoluminescence (CL) measurements were performed on a Zeiss ULTRA55 field-emission scanning electron microscope (SEM) equipped with a Gatan MonoCL3 system. An electron beam with an energy of 5 keV and current of 0.4 nA was used for these measurements.

The samples were commercially available NaCl crystals with 99.99% purity from Merck Millipore and NaCl cell windows from Sigma-Aldrich, which were cleaved and cut to the needed size.

III. RESULTS AND DISCUSSION

We created a luminescent pattern on a NaCl crystal by implantation of roughly 6500 helium ions per pixel using a
20 nm pixel separation and irradiating only a predefined area. Later, the patterned area was imaged using ~1600 ions per pixel (4.5 pA beam current and 58 µs dwell time) using the same pixel separation. The obtained panchromatic IL and SE images are shown in Figs. 1(a) and 1(b), respectively. The IL image clearly shows the created pattern (Fig. 1(a)). The SE image in Fig. 1(b) does not show any surface damage. The vague contrast in the SE image is the result of charging effects.

The patterned structures luminesce not only under ion irradiation. In order to demonstrate this, a similar pattern using identical irradiation conditions had been created in a cleaved NaCl cell window and was then investigated by CL using a SEM. SEM is a less destructive technique as compared to HIM. This allows the usage of higher beam currents and, consequently, generation of larger luminescence signals with a better signal-to-noise ratio compared to IL. A panchromatic CL image of the pattern is shown in Fig. 1(c). The bright spots in the image are small NaCl crystal fragments on the surface which are the result of poor crystal cleavage. Either an unanticipated sample drift during patterning or surface charging effect caused the discrepancy between the desired (see insets in Figs. 1(a) and 1(c)) and obtained patterns.

Although an energetic ion beam preserves its shape in the surface vicinity, the beam profile broadens within the material due to nuclear collisions. Additionally, the actual interaction volume relevant for IL is not restricted by the size of the ion induced collision cascades. The generation of electrons also has to be taken into account. For example, the width of the letter “I” in the pattern in Fig. 1(a) is ~1.16 µm, whereas, the desired width was only 1.0 µm. The minimal possible lateral pattern size is limited by the beam interaction volume with the material. This gives rise to the discrepancy in the anticipated and actual ratio line width of the pattern.

While SE images in HIM provide a high surface sensitivity due to the short electron escape depth, the IL signal contains bulk information. The IL images are a projection of the concentration of light emitting centers on the sample surface. Therefore, IL imaging allows the direct visualization of the beam interaction volume diameter. Since the ion beam diameter is below 0.5 nm, we can neglect the actual beam profile and treat the situation as a single point impact. An example of the direct measurement of the lateral size of the interaction volume of the He⁺ beam with the NaCl crystal is presented in Fig. 1(d). We created an array of single pixel impacts applying different amounts of He⁺ ions by varying the ion beam current and dwell time ranging from 0.8 pA to 6.6 pA and 100 µs to 4000 µs, respectively. Later, the patterned areas were imaged with a resolution of 1024 × 1024 pixels, a beam current of 0.5 pA, and a dwell time of 58 µs, corresponding to ~200 He⁺ ions per pixel. Alternatively, CL imaging could be used. However, one would need to tune the electron beam energy to be able to probe the sample at the depth which corresponds to the range of He⁺ ions in NaCl. In this case, even if CL is able to provide the required lateral resolution, the difference in the depth profiles of the ion- and electron-matter interaction volumes would introduce an additional new uncertainty to the obtained results.

In Fig. 1(d), each of the four bright spots in the IL image is a single pixel ion beam impact, but after different amounts of helium were implanted. In the shown example, the doses were: 7340, 14 680, 22 020, and 29 360 ions per pixel starting from the top left to the lower right corner. Using Fiji, the spot radii were extracted from the images for a deposited charge ranging from 0.2 fC (1.2 × 10⁶ ions) to ~20 fC (1.2 × 10⁷ ions). The IL intensity profiles were radially averaged and could be fitted by a Gaussian distribution function with high accuracy (Fig. 2). The values of the spot radii were taken at the gray level equal to the mean noise level plus twice the standard deviation of the noise. The obtained dependence of the spot radius on the amount of incident ions is shown in Fig. 3.

The central part of the IL spot is difficult to predict and describe due to the high defect concentration. The defects may interact and cluster and, thereby, affect the produced IL signal in a hard to predict way. The outer part of the IL profile corresponds to a low defect concentration and should show a linear response to the increase of the ion dose. We, therefore, assume that the edge of the IL spot profiles can be described by a Gaussian function with the center at the point

FIG. 1. (a) and (b) IL and SE images of a pattern on a NaCl crystal. The He⁺ beam energy is 35 keV. Field of view (FOV) is 18 µm × 10 µm. (c) Panchromatic CL image of a pattern created on a cleaved NaCl crystal in HIM. FOV is 25 µm × 14 µm. (d) Panchromatic IL image of a NaCl crystal surface after a “four-pixels” patterning with a 35 keV focused He⁺ beam. Beam current was 4.7 pA. Dwell times, moving by rows from top left corner to the lower right corner: 250 µs, 500 µs, 750 µs, and 1000 µs. For imaging, current of 0.5 pA and dwell time of 58 µs were used. The insets in (a) and (c) demonstrate the desired pattern.
of incidence, and a common standard deviation. We can write the following expression:

\[ \frac{nI}{\sigma \exp \left( -\frac{r^2}{2\sigma^2} \right)} = S, \]  

(1)

where \( I \) is the amount of incident ions, \( r \) is the spot radius, \( \sigma \) is the standard deviation, \( x \) is a scaling constant, and \( S \) a threshold value to obtain a measurable IL signal. From this expression, we arrive at the following dependence of the spot radius on ion dose:

\[ r = \sigma \sqrt{2lnI-B}, \]  

(2)

where \( B = 2ln(\sigma S/x) \).

The experimental data were fitted with Eq. (2). The obtained fit is presented in Fig. 3 as a blue line. The \( \sigma \) value extracted from the fit is \( 88.3 \pm 1.5 \) nm. It reflects the distribution of the defects generated by the ion beam (or, to be more precise, of the emitting centers).

The interaction of ions with matter and the associated defect generation is typically simulated using stopping and range of ions in matter (SRIM).\(^{23} \) According to SRIM, the calculated radial range of 35 keV He\(^+\) ions in NaCl is 175 nm. However, this is a fixed value which does not depend on the ion dose. To predict the dose dependence, we simulated the vacancy distribution. The SRIM output in a form of the 3D vacancy distribution contains a projection of the vacancies on a plane which is perpendicular to the surface. However, we are interested in a cross-section of the projection on the sample surface. To extract this cross-section, we processed the full collision data containing details about the generated recoils. The extracted vacancy profile differs from the experimental spot profile (Fig. 2). It has an extremely high defect concentration at the point of incidence which subsequently rapidly decreases with increasing radial distance.

We used the vacancy distribution profiles obtained from SRIM to estimate the minimal defect concentration needed for the generation of a measurable IL signal and to predict the spot radius dependence on the ion dose. The vacancy profiles were calculated for different ion doses. From these profiles, we extracted the radial distances which correspond to a fixed number of vacancies (Fig. 2). The determined correlation between ion dose and spot radius is compared to the experimental data in Fig. 4 (green circles and line—SRIM simulation, and red squares—experiment). The SRIM simulation predicts the correct shape of the interaction volume radius dependence of the ion dose. The number of vacancies was varied to obtain the best fit to the experimental data. The best fit was obtained for 3 vac/nm\(^2\), which corresponds to about 17 vacancies per pixel. Please note, that these vacancies are distributed in a direction perpendicular to the surface over the interaction volume. Also note that, although we use a low ion dose for pattern imaging, in each pixel, the IL signal is collected from a volume which is bigger than the defined pixel size. The experimentally obtained profile is a convolution of the actual defect distribution profile with the probe profile. The influence of the non-zero size of the probe is more significant at low ion doses, where the spot radii are

![FIG. 2. IL intensity radial profiles of single pixel impacts of a 35 keV focused He\(^+\) beam into NaCl. Number of implanted He\(^+\) ions: 7500 ions (blue line) and 58 750 ions (black line). The experimental profiles are fitted with Gaussian curves. The dashed vertical lines indicate the spot radius at the gray level equal to the mean noise level plus twice its standard deviation. The pink and cyan dash-dotted lines are vacancy density profiles from the SRIM simulation for 7500 ions and 58 750 ions, respectively. The black dashed horizontal line indicates the radius which corresponds to 3 vac/nm\(^2\).](http://scitation.aip.org/content/aip/journal/jap/115/18/10.1063/1.4875822)

![FIG. 3. Dependence of the radius of the luminescent area on the amount of the incident He\(^+\) ions. The beam currents were 0.8 pA, 1.2 pA, 4.7 pA, and 6.6 pA. The dwell time was varied from 100 \( \mu \)s to 4000 \( \mu \)s. Green squares correspond to the data points from the measurement presented in Fig. 1(d). The blue solid line is the fit by the function from Eq. (2).](http://scitation.aip.org/content/aip/journal/jap/115/18/10.1063/1.4875822)

![FIG. 4. Comparison of the SRIM simulation (green circles and line) and calculated point spread function (solid blue line) with the experimentally measured radius of the interaction volume (red squares).](http://scitation.aip.org/content/aip/journal/jap/115/18/10.1063/1.4875822)
small. Thus, the IL spot radius is overestimated at these doses (see Fig. 3). At high ion doses, SRIM overestimates the radial distance since it does not take into account helium implantation. Implanted helium acts as an efficient trap for incoming helium ions and, in this way, affects and reduces the average ion range.

Winston et al.,24 have combined SRIM and electron generation using a Monte Carlo method for simulation of the point-spread function (PSF) in HIM. The PSF provides a spatial distribution of the energy dissipation for a single point impact.25,26. The software developed by Winston et al.25 was used to simulate the impact of a 35 keV He+ beam on a NaCl crystal. We used 105 helium ions and a 750 nm thick NaCl slab for the simulation. The simulation describes the dissipated energy per volume unit and ion as a function of the radial distance from the impact point. To be able to compare the simulation with the experimental results, the units were converted into an inverse ion dose [fC−1]. To do so, we used the sum of the electronic and nuclear stopping powers which were extracted from the SRIM simulation at several depths and averaged within 25 nm thick slabs. Due to the bulk nature of the IL signal, we are interested in the dissipation of the energy over the whole slab. The PSFs for all 25 nm slabs were then summed up to obtain the projection of the total dissipated energy on the surface. This is different from the simulation in Ref. 24 where the PSF was extracted only for a single thin sample layer in direct vicinity of the surface. The comparison of the simulated PSF with the experimental results is shown in Fig. 4 (blue solid line). Two Gaussians are the main contributions into the PSF.24,25 The first term smear out with increasing depth as a result of the increase in nuclear stopping power. The bigger importance of this term in our calculation for a bulk like sample is the reason for the difference in the shape of the present simulation and the one in Ref. 24. The PSF clearly underestimates the spot radius. This is due to the fact that the PSF calculation does not take into account the generation of recoils. According to the SRIM simulation, nearly half of the generated vacancies are created by the recoiling target atoms. This influences the spatial distribution of the energy dissipation. Moreover, we do not observe a significant difference in shape between the PSF and the curve obtained from SRIM. This is because of the short electron mean free path of only 1–2 nm in NaCl.27,28 Unfortunately, we do not have experimental data for radial distances smaller than 40 nm. For the corresponding small ion doses, the IL signal becomes hardly distinguishable from the background. On the other hand, extremely high ion doses could also not be applied in order to avoid significant sample modifications due to material sputtering and helium implantation.29 Additionally, the charging of the sample surface leads to deflection of the beam at high ion doses.

IV. CONCLUSION

We have directly visualized and measured the lateral size of the interaction volume of a 35 keV He+ beam with NaCl using the ionoluminescence technique. The characteristic length scale of the radius of the volume containing emission centers was found to be 88.3 ± 1.5 nm. SRIM and PSF simulations were used to predict the dependence of the interaction volume radius on the ion dose. Although these are simplified models for the damage simulation and do not take into account defect interaction and diffusion, both lead to a good agreement with the experimental data. The SRIM simulation predicts a surface projected defect concentration of 3 vac/nm2 at the edge of the luminescent spots visualized with IL. The PSF calculation underestimates the values of the spot radius since it does not consider generation of recoils. Moreover, in the material of interest, the PSF calculation does not provide additional information due to the short electron mean free path. We have further demonstrated the possibility to locally change material properties with very high precision in HIM. In the current work, we altered the luminescence properties of the material, but possibly magnetic, electronic, and other properties can be modified too.

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