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The center for production of single-photon emitters at the electrostatic-deflector line of the Tandem accelerator of LABEC (Florence)

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ABSTRACT

The line for the pulsed beam of the 3 MeV Tandetron accelerator at LABEC (Florence) has been upgraded for ion implantation experiments aiming at the fabrication of single-photon emitters in a solid-state matrix. A system based on Al attenuators has been calibrated in order to extend the energy range of the implanted ions from MeV down to the tens of keV. A new motorized XY stage has been installed in the implantation chamber for achieving ultra-fine control on the position of each implanted ion, allowing to reach the scale imposed by lateral straggling. A set-up for the activation of the implanted ions has been developed, based on an annealing furnace operating under controlled high-vacuum conditions. The first experiments have been performed with silicon ions implanted in diamond and the luminescent signal of the silicon-vacancy (SiV) center, peaked at 738 nm, has been observed for a wide range of implantation fluences ($10^8 \div 10^{15}$ cm^{-2}) and implantation depths (from a few nm to 2.4 μm). Studies on the efficiency of the annealing process have been performed and the activation yield has been measured to range from 1% to 3%. The implantation and annealing facility has thus been tuned for the production of SiV centers in diamond, but is in principle suitable for other ion species and solid-state matrices.

1. Introduction

Color centers in a solid-state matrix, like diamond or silicon carbide, are highly promising candidates for the generation, storage and processing of single photons. The intrinsically narrow spectral linewidth at room temperature, the photon emission rate, the coherence time, as well as their photostability even at large temperatures [1], make these systems among the most likely to be employed as a hardware substrate for quantum information [2–6].

Only a few approaches are currently used to introduce single color centers in a solid substrate, i.e. post-growth diffusion of impurities deposited on the surface, introduction of impurities either in the gas feed or in the melt during crystal growth and ion implantation [7–9]. Post-growth diffusion is not viable when the diffusivity of the ion species is too low (as common in diamond substrate), while doping during growth of the material, though resulting in a relatively defect-free doped crystal, gives no control on the position of the induced defects on the growth planes.

Ion implantation followed by proper thermal activation allows overcoming both the above-mentioned drawbacks of the other techniques. In fact, it provides a most often viable approach and it allows fine control, within the limit of longitudinal and lateral straggling, over the position of the centers in three dimensions. The implantation depth can be tailored to the specific application by varying the energy of the ions. The depth resolution, being only limited by the width of the Bragg peak, ranges from nanometers (for keV ion implantations) to hundreds of nanometers (for MeV ions). Regarding the lateral position, any desired point can be chosen by simply changing the beam impact point on the sample, either by displacing the beam over the sample or by moving the sample under the beam. Both approaches are possible, the former being typically preferred for high precision positioning, even though ultra-high precision stages are getting more and more common and economically affordable. By displacing the beam, it is possible to change the implantation point typically within an area of the order of few

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square millimeters, while much wider areas can be covered by moving the sample. Whatever the adopted solution, however, the lateral resolution is limited either by the beam width (down to hundreds of nm for high intensity beams and to few tens of nm for low intensity ones) or by the mask aperture (down to nanometers with current lithographic techniques) and by lateral straggling [10,11]. The latter contribution can vary from hundreds of nanometers to few microns, depending on the ion-energy combination and the target; just to refer to typical conditions for implantations in diamond, the lateral straggle is about 700 nm for 2 MeV protons, 120 nm for 11 MeV nitrogen ions or for 10 MeV silicon ions.

The main drawbacks of ion implantation are: i) the generation of a relatively high number of structural defects (mainly vacancies); ii) the limited activation yield of the implanted centers, which can be as low as a few percent [12] (e.g. for SiV) or as high as 80% [13] (for NV centers) depending on the ion species and the activation procedure. For the very low fluences required in the fabrication of single-photon emitters, vacancy generation is not a real issue due to the intrinsically high vacancy density of the pristine chemical vapor deposited (CVD) crystals, which can be as high as 10^{18} cm^{-3} [14].

Moreover, if the color center is a complex, the presence of a certain amount of structural defects could be a factor favoring the activation of the centers. This is the case of the nitrogen-vacancy (NV) and the silicon-vacancy (SiV) centers in diamond, both being formed by the complex composed by a doping atom and a lattice vacancy. In these cases, in order to improve the activation yield of the centers, generation of a controlled amount of defects by damaging the lattice with carbon or proton beam has been performed, with limited success [15], while femtosecond laser micromachining followed by proper annealing is emerging as a promising technique [16].

Either in the case of simple substitutional doping or of complexes, the activation of color centers requires proper annealing in order to allow the implanted ions, usually in interstitial positions, to bond with one or more vacancies or other species by diffusion of both vacancies and interstitials. Annealing is also profitable in order to restore the lattice damaged by implantation, because of the recombination of vacancies and interstitials. In diamond, diffusion of vacancies [17] occurs only above about 800 °C, while interstitials can move also at room temperature [18]. In order to favor Frenkel couples recombination and to avoid formation of vacancy complexes, annealing procedures, alternative to simple post-implantation heating at 1000–1200 °C, have been implemented. Namely, implantation in hot diamond (~800 °C), leading to instantaneous annihilation of the point defects, and cold-implantation (liquid nitrogen temperature), intended to prevent complex formation, followed by *in situ* rapid annealing at about 1000 °C (Cold Implantation – Rapid Annealing: CIRA) [19]. The efficacy of these alternative annealing schemes largely depends on the application and is questioned in some cases. For instance, CIRA is effective in p-doping of diamond by boron implantation, while in phosphorus doping it has not yet given reproducible results [20]. The other limit of the implantation technique, as well as of all the other methods, is the random activation and orientation of the centers. This seems to be addressable only by the implementation of defect-tolerant architectures [21], which are beyond the present state-of-the-art capabilities.

The relative alignment of color centers is important for the deterministic arrangement in an array, which is one of the crucial goals of these studies. At present, ultra-high spatial resolution implantations tend to prefer low energy facilities, typically using particles with energies from few keV to tens of keV, although hundreds of keV and even MeV energies are also reported. Recently, keV ion implantation has achieved extraordinary spatial resolution and is now possible to focus ion beams down to the nanometre and sub-nanometre sizes on the sample surface. These probes are of great interest for high resolution biological imaging [22] and for the fabrication of nano-structures [23], such as Josephson devices in YBaCuO films with 2 nm lateral resolution [24] and deterministic implants of dopant atoms [25,26]. In the latter case, to achieve the required precision, nanostencil masks (30 and 60 nm wide) have been used [27]. Particle beams in the range of hundreds of keV have proved the feasibility of high spatial resolution and in a recent study [28] an experimental configuration has been proposed, aiming to produce sub-10 nm direct write lithography with a 200 keV proton beam in films whose thickness is well below the ions range. Furthermore, the recent years have witnessed the development of MeV ion beams with extraordinary high spatial resolutions, so that dimensions well below 100 nm are now feasible, and spot sizes within 20 nm for proton and alpha particle beams have been measured since 2013 [29].

It is worth noting that the high spatial resolutions of these beams can be maintained through the first micrometer or so for light Z matrices, such as diamond, where the energy deposition profiles of the ions are laterally constrained to a few nanometers from the initial ion path. This is not beneficial for the ion implantation itself (which requires to reach the ion end-of-range), but is advantageous when the aim is to generate vacancies which should enter in the formation of the color centers. This could be the case, for instance, of an implantation of Si ions at relatively low energy followed by carbon irradiation at higher energy and fluence, so that the vacancy distribution around Si atoms is artificially increased. In this case, the overall resolution of the SiV formation process is driven by the higher of the two: either the Si implantation or the vacancy generation. Studies exploiting samples thinner than the range of the beam particles [30] have been carried out in recent times to explore the effects of damage before end-of-range.

A further attractive feature of ion implantation is the possibility of using pulsed beams, which adds the fine control over the number of implanted ions to the capability of introducing the ions in the desired position along the three directions. Actually, the average number of ions per bunch can be reduced down to even less than a single ion, thus opening the way to a true deterministic implantation [31] of a specific number of ions in the desired position, whose importance for the future fabrication of integrated monolithic devices is apparent.

Facilities exploiting electrostatic deflectors to gain a fine control over the number of particle delivered to the sample, either implanted or transmitted, have been reported over the years (see for example Refs. [32–35]) and continue to be highly attractive for applications in diverse fields, mainly in biology and material science [36,37].

Here, we discuss the fabrication of single-color centers, capable of emitting a single photon at a time, by diamond implantation carried out by using pulsed beams at the electrostatic deflector facility DEFEL (ELectrostatic DEFlector).

We have developed the system having in mind a flexible, general-purpose implantation facility useful in the prototypical phase of a vast class of photonic devices. A sputter ion source provides virtually every kind of ion in reproducible and controlled implantation conditions; The double-deflector system extends the range of the possible fluences over 7–8 orders of magnitude (10^{8}–10^{15} cm^{-2} or more); calibrated metal energy attenuators allows to explore the range of implantation energies from tens of keV to tens of MeV. Flexibility in energy permits the creation either of shallow centers in a planar configuration or of deeply immersed color centers in a micro-lenticular structures or in photonic cavities. The limit in precision due to lateral straggling, which ranges from 50 to 80 nm for depths in the interval 0.5–1 μm (for Si ions, calculated by SRIM), is tolerable for most of the foreseen applications. The implantation at average-depths could also allow for ablation of the superficial layers, sometimes affected by damage induced by the annealing process. Flexibility in fluence and the possibility of an easy change of the ion-species allows for implantation of low-fluence Si or N ions (for instance) and then the high-fluence implantation of carbon, at a different energy, in order to artificially increase the defect concentration, to improve the activation yield. In the experiments performed and briefly reported in the manuscript to demonstrate the feasibility of single color center creation, we have explored only some of these potentialities, which make our system a powerful facility to