A compact, ultra-high vacuum ion source for isotopically enriching and depositing $^{28}\text{Si}$ thin films

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An ultra-high vacuum (UHV) compatible Penning ion source for growing pure, highly enriched $^{28}\text{Si}$ epitaxial thin films is presented. Enriched $^{28}\text{Si}$ is a critical material for quantum information due to the elimination of nuclear spins. In some cases, the material must be grown by low temperature molecular beam epitaxy (MBE), e.g., scanning tunneling microscopy (STM) hydrogen lithography-based devices. Traditional high-purity physical vapor methods typically deliver a very small fraction of source material onto the target substrate, making the cost for use with highly enriched source materials very high. Thus, directed beam sources provide an efficient alternative. This UHV Penning source uses all metal or ceramic parts and a removable electromagnet to allow bake-out. The source gas is commercial (natural isotope abundance) silane gas (SiH$_4$), an inexpensive source material. High enrichment levels up to 99.99987% (8.32 $\times$ 10$^{-7}$ mol/mol $^{29}\text{Si}$) and high chemical purity of 99.965% are shown without post-processing. We present and discuss the discharge properties of this new source, the ion mass spectrum when coupled to our mass filter, and the secondary ion mass spectroscopy (SIMS) of the grown films.

I. INTRODUCTION

Isotopically enriched silicon based qubits that utilize electron and/or nuclear spins in quantum dots and/or donors are competitive candidates for quantum computation (or memory) due to very long coherence times \cite{1,2} and high gate fidelities \cite{3,4}. Compared to natural abundance silicon, the coherence times increase orders of magnitude when using isotopically enriched $^{28}\text{Si}$ as host material. Natural silicon contains $\approx$ 4.7% $^{29}\text{Si}$ (nuclear I = $\frac{1}{2}$), which causes random fluctuations and inhomogeneities in the background magnetic field and dramatically reduces the qubit coherence time. By reducing the $^{29}\text{Si}$ nuclear spin density to < 0.005%, nuclear spin coherence times ($T_{2n}$) approaching an hour \cite{5} and electron spin coherence times ($T_{2e}$) exceeding a second \cite{6} have been reported in $^{28}\text{Si}$ using $^{31}\text{P}$. 
Despite the advantages of isotopically enriched $^{28}\text{Si}$, the supply is very limited, due largely to the extreme cost of enriching silicon. Perhaps the most highly enriched single crystal bulk $^{28}\text{Si}$ is from the International Avogadro Project [7], which was produced using centrifuge enriched gaseous silane and a long process chain resulting in zone refined, single crystal silicon with a residual $^{29}\text{Si}$ isotope fraction of about $10^{-5}$ mol/mol [8]. The end goal in that case was to produce a macroscopic artifact ($\approx 1$ kg) of enriched silicon for metrological purposes. Quantum information applications do not require macroscopic quantities of $^{28}\text{Si}$ for each device, so an alternative, less expensive strategy has been to grow epitaxial $^{28}\text{Si}$ layers on natural silicon substrates using enriched silane gas. For example, chemical vapor deposition (CVD-grown) $^{28}\text{Si}$ epilayers grown on 300 mm$^2$ substrates that is enriched to 99.992 % [9]. Remnants from other sources [10] of $^{28}\text{Si}$ also exist, providing access for research efforts, typically with enrichments $\leq$ 99.9 % $^{28}\text{Si}$, including the float-zone grown samples from Keio University [11], CVD grown thin films at Princeton University [12], solid-source molecular beam epitaxy (MBE) grown thin films at Technical University of Munich (TUM) [13], ion beam method from Penning source based ion implanter [14], etc. Generally, these isotopically enriched $^{28}\text{Si}$ materials are not extremely enriched ($\approx 99.9$ % $^{28}\text{Si}$), are of very limited quantity, and are not being replenished.

In addition to the general need for high quality $^{28}\text{Si}$ for quantum information sciences (QIS), additional experiments are needed to determine the detailed relationship between enrichment and quantum coherence. The exact value of enrichment required for QIS remains unknown. An ideal solution would be to produce enriched silicon with many, different targeted enrichment levels and systematically assess the performance (e.g., coherence time) of a test device. In theory work, Witzel et al. predicted that with every order of magnitude increase in isotopic enrichment, the coherence time will increase approximately an order of magnitude [15], but emerging experiments have indicated performance with enrichment (0.08 % $^{29}\text{Si}$) better than predicted, motivating additional studies [2, 16]. Therefore, a source of $^{28}\text{Si}$ that can produce targeted enrichment levels spanning a wide range would enable mapping of the decoherence time and provide specifications for large-scale enriched silicon production.

We have previously reported on our ability to make very highly enriched $^{28}\text{Si}$, where we used a Penning ion source to ionize natural abundance SiH$_4$ gas, mass filtered the ions, decelerated to hyperthermal energies, and deposited isotopically enriched $^{28}\text{Si}$ \textit{in situ} [17],[18],[19]. Using this
method, enrichment of $^{28}\text{Si} > 99.99983\% \ (< 10^{-6} \text{ mol/mol } ^{29}\text{Si})$ was achieved. This is the highest $^{28}\text{Si}$ enrichment known to be reported so far. However, the chemical purity of the silicon films using this ion source was poor (98.47%). Specifically, SIMS (secondary ion mass spectroscopy) was used to determine the dominant chemical impurities of carbon (C), oxygen (O) and nitrogen (N). Our prior system analysis assumed only background impurities in the growth chamber could be incorporated, however, mass 28 u impurities mixed into the silane source gas in the inferior vacuum region of the ion source were also transported ballistically (not just diffusively) along with the silicon ion beam, due to their similar molecular mass. For example, $\text{N}_2^+$, $\text{CO}^+$ and other mass 28 u ionized compounds such as $\text{C}_2\text{H}_4^+$ and $\text{CNH}_2^+$ can pass through our mass selector to the sample since our mass resolution does not discriminate at that level ($< 0.03$ u).

Therefore, here we target the vacuum condition of the ion source area for improving the chemical purity of our films. Our prior Penning source was not ultra-high vacuum (UHV) compatible. It used rubber O-rings for vacuum seal and plastics for high voltage isolation with a base pressure of $\approx 2.7 \times 10^{-6} \text{ Pa} \ (\approx 2 \times 10^{-8} \text{ Torr})$. Consequently, the $^{28}\text{Si}$ films grown using that ion source had C concentrations in the range of $10^{20} \text{ cm}^{-3}$, and O and N concentrations in the range of $10^{19} \text{ cm}^{-3}$, respectively. This impurity level is a problem for device fabrication (e.g., high quality oxide growth) and can potentially also act as a source of decoherence for qubits in silicon $^{[20,21]}$. Therefore, a new UHV ion source is needed to eliminate residual gases in the ion source and the chemical impurities in the $^{28}\text{Si}$ film.

As described above, the system with the newly designed UHV ion source must produce highly enriched $^{28}\text{Si} \ (< 10^{-6} \text{ mol/mol } ^{29}\text{Si})$ and improved chemical purity ($< 10^{18} \text{ cm}^{-2}$ impurities). The specific goals for this work are: 1) to reduce ionization source base pressure to $< 3 \times 10^{-8} \text{ Pa} \ (\approx 2 \times 10^{-10} \text{ Torr})$ to similarly increase the film chemical purity; 2) to identify the source’s optimum operating conditions for epitaxial thin film deposition; and 3) to enrich epitaxial $^{28}\text{Si}$ thin films to $< 10^{-6} \text{ mol/mol } ^{29}\text{Si}$. In this paper, we present the details of our new ion source able to achieve these goals, present the data and discuss these performance metrics.

II. EXPERIMENTAL SETUP

The design of our UHV ion source is described below. In addition to achieving ultra-high vacuum, this UHV ion source must also be compatible with the existing ion transport, mass filter and deposition system. The details of the associated system can be found elsewhere $^{[18]}$, however,
a brief description is presented here to assist understanding. The enriched silicon system consists of four subsystems: the gas handling, the ionization source, ion transport, and the deposition chamber, which is additionally coupled to a load lock and a scanning tunneling microscope (STM) chamber that will not otherwise be discussed here. The ion source is a Penning-type ion source [22], which has a cylindrical anode and cathodes at each end that creates an axial confining potential well. The ion’s radial confinement is provided by an axial magnetic field from an electromagnet, which also helps focus ions for extraction. During the discharge, a plasma is formed by accelerating electrons from the cathodes that ionize the gas molecules. SiH₄ is used in this case, although Ar and Ne have also been used for diagnostics. Ions are extracted using an extraction cusp adjacent to one end of the source and transmitted into a system of electrostatic lenses. Since we require hyperthermal energy ions (< 50 eV kinetic energy) that are susceptible to Coulomb repulsion (space charge) effects [23], the transport system is typically operated at -4 kV (i.e., ions are accelerated to > 4 keV while transiting the lenses and mass filter) and decelerated before deposition. As a result, high voltage isolation between the ion source and the rest of the systems (transport and gas inlet) is required. In the prior ion source, a plastic transition plate was used as electric isolation and was one of the major causes of poor vacuum. In the new design, we use an 8” CF reducer nipple with ceramic neck to mate the ion source to the transport system and use ceramic standoffs for the gas inlet, as shown in Fig.1.

Apart from the compatibility with the existing system, several other factors constrain the design of this UHV ion source. First, all components need to be UHV (< 1.33 × 10⁻⁷ Pa or 10⁻⁹ Torr) compatible and bakeable (> 150 °C), including the gas injection. Therefore, all tubes from the SiH₄ gas bottle to the ion source feedthrough use vacuum coupling radiation (VCR) fittings to prevent air (C, O, N rich) from leaking into the gas line. Second, all plastics components such as polytetrafluoroethylene (PTFE) and nylon are replaced with ceramics. Plastics can contribute fluorine and chlorine compounds, as well as lighter gases, and present problems when the ion source becomes hot during baking. Third, the prior ion source’s electromagnet was buried inside the housing without efficient cooling. Heating of the electromagnet caused outgassing and source instability, the wire insulation commonly failed, and baking was not possible. In the new design, the magnet is a separate component outside the vacuum system, water-cooled and removable for baking. Furthermore, to ease replacement of the anode and cathodes, the core of the ion source can be easily taken in and out without disturbing the magnet or other elements. Finally, the new
A schematic of the UHV Penning ion source is shown in Fig.1 and discussed in detail below. Our design goal was to keep the ion source dimensions as compact as possible and fully supported by the 70 mm CF base flange, while also having > 5 kV electrical isolation between the anode and the cathodes. The ion source is shown in Fig.1 with dimensions and geometry correct according to the scale bar. The ion source’s plasma region has three main consumable components shown as dark red: the anode, cathode and anti-cathode inserts. The distance between the cathodes and the anode is based on Ref. [24], where the performance of the gas discharge has been optimized. The anode, cathode and anti-cathode supports are 304 stainless steel (SS). The cathode inserts are constantly eroded by ions during plasma discharge and this design allows the anode and cathode inserts to be replaced easily, minimizing the maintenance steps and time. The lifetime of the cathodes depends on material type, gas source and energy of the impact, but typical insert lifetimes are about 30 h.

For the purpose of hyperthermal (5 eV to 100 eV) $^{28}$Si epitaxial thin film growth, the plasma potential and the final energy of the ions are approximately set by the anode voltage [18], which is typically set to be around 50 V. The hyperthermal energy range allows atoms to land softly onto the substrate during deposition, optimizing the $^{28}$Si island density and crystalline quality without introducing point defects [18].

The high voltage feedthroughs and the gas inlet are also shown on the base flange at right. The anode and cathode supports are connected by small copper wires that pass through thin insulating tubes to the feedthroughs and are fixed with vented screws (to prevent virtual leaks). Ceramic rings and top hat washers are inserted to provide electrical isolation between cathodes and anode, which typically have a 3 kV potential difference, and to maintain good geometric alignment. The main body (vacuum wall) is designed to be at the cathode potential (copper standoffs) or at a different potential, e.g., earth ground (ceramic standoffs—shown). For example, using ceramic standoffs allows the ion source body to be grounded so that a mass flow controller can be installed to provide precise control of the gas flow. Under some circumstances, the plasma power can substantially heat the central components leading to high voltage breakdown, which can be better mitigated with the copper standoffs that conduct heat away efficiently.
III. RESULTS AND DISCUSSIONS

The discharge properties of this UHV ion source using SiH₄ gas are studied to determine the optimum operation conditions. The arc (plasma) current and the total ion beam current extracted from the ion source are affected by the ion density and the electron temperature of the discharge, and those quantities are influenced by the arc voltage, flow rate and source magnetic field [24]. In Fig.2, the total $^{28}\text{Si}^+$ ion current and arc current are shown as functions of these three parameters.

The measurements were done by first maximizing the ion current while changing source magnetic field and flow rate at -2.7 kV arc voltage. These values of magnetic field and flow rate are then marked as optimum values $H_{\text{opt}}$ and $F_{\text{opt}}$ in Fig.2. Then, each of the three parameters is uniaxially varied while the other two are kept constant at their optimum values.

The ion and arc current dependence on arc voltage is shown in Fig.2(a). The discharge begins at around -1.7 kV and the ion current increases monotonically with the arc voltage up to a first maximum at -2.7 kV, and then shows weak structure suggestive of higher order plasma modes at -3.4 kV and -3.8 kV. The arc current shows a similar trend but reaches a maximum at -2.4 kV and has weaker mode structure. In Fig.2(b), the ion current versus source magnetic field is shown while keeping the arc voltage at -2.7 kV and the gas flow at -0.02 sccm. The plasma ignites at about 0.6 T and the total ion current increases rapidly reaching a maximum at 0.67 T. Here the mode structure is more pronounced with two other ion current maxima appearing at 0.77 T and 0.86 T. The arc current again shows a similar trend to the ion current, where three somewhat weaker, corresponding maxima are observed. The variation of the ion current vs. the flow rate while keeping the arc voltage at -2.7 kV and the magnetic field at 0.77 T is shown in Fig.2(c). Unlike in arc voltage and source magnetic field, the ion current vs. flow rate shows a large peak at 0.02 sccm and a softer, broader peak at 0.11 sccm. The arc currents increase monotonically after ignition over the entire range studied. The optimum operating condition for $^{28}\text{Si}$ deposition using SiH₄ gas is therefore at -2.7 kV arc voltage, 0.77 T source magnetic field and 0.02 sccm (1.87 × 10⁻⁴ Pa or 1.4 × 10⁻⁶ Torr) flow rate. These values closely match those of the previous ion source on which this source was based [24].

Having discussed the plasma performance of the ion source, we now move on to evaluating the improvements in gas cleanliness and efficacy for silicon enrichment that motivate this effort. To effectively enrich the silicon, once the ion source is coupled to the beamline [18], the transmitted
silicon ions must have trajectories well separated from each other when sweeping the magnetic
field of the ion mass separator in the beamline. This allows one mass to be selected by the
separator aperture while rejecting other masses. The mass spectra of the silicon ion beam taken
with the prior and UHV ions sources are compared and shown in Fig. 3(a). The ion mass
spectrum is collected using a second, custom aperture plate on the sample stage to monitor the
ion current while scanning the magnetic field of the mass analyzer. Six singly charged SiH₄
related peaks are shown. The first peak at mass 28 u corresponds to ²⁸Si⁺ ions, while the rest of
the peaks result from a combination of isotopes and hydrides due to the incomplete cracking of
SiH₄ gas molecules. In ion beam deposition, the enrichment is dominated by the mass separation
between mass 28 u and 29 u peaks (See ref. [17] for detailed analysis of mass selectivity). The
UHV ion source’s similar peak shape and separation compared to the prior source indicate good
mass selectivity for enrichment, and similar current suggests a similar growth efficiency with this
ion source. Typically, we use a deposition rate of 0.99 nm/min and the ion source is stable
throughout the deposition (usually 6 h to 8 h). Higher growth rate might be achieved by using
different plasma modes (e.g. higher flow rate), but generally results in shorter cathode lifetime
and larger surface roughness of the deposited film.

The enrichment expected from the mass spectrum is verified in Fig.3(b) using SIMS (secondary
ion mass spectroscopy) to profile the isotopic fraction of ²⁸Si, ²⁹Si and ³⁰Si of the deposited ²⁸Si
film grown using this UHV ion source. The SIMS measurement was taken near the center part of
the enriched silicon film, which is usually the thickest. The residual isotope fraction of ²⁹Si is
shown as squares with an average value of 8.32(80) × 10⁻⁷ mol/mol in the film and ³⁰Si is shown
as triangles with an average value of 4.91(65) × 10⁻⁷ mol/mol. The ²⁸Si total enrichment for this
sample is 99.99987(3) %. The enrichment level can vary some from run to run, but comparing
several samples deposited using the prior ion source with samples from this ion source, we
conclude that the ²⁸Si enrichment is maintained with this UHV ion source.

Since the growth chamber pressure is typically maintained at 6.7 × 10⁻⁹ Pa (5 × 10⁻¹¹ Torr), the
background gas composition in the ion source was the leading contributor to film contamination
in the prior source and the primary motivation for building a UHV ion source. The baseline
pressure as measured with an ion gauge (uncertainty of 10 % to 20 %) has been improved by a
factor of a hundred in this UHV ion source compared to the prior ion source, now reaching 2.7 ×
$10^{-8}$ Pa ($2 \times 10^{-10}$ Torr). The partial pressures of various gas components as measured by a residual gas analysis (RGA) in the prior and UHV ion sources are shown in Fig.4(a) and Table I. These show the qualitative improvement in vacuum conditions and chemical compositions and confirm that the impurities contributed from the ion source vacuum have been reduced by a factor of 100.

A SIMS depth profile showing the chemical impurity concentrations for C, N, O, F and Cl in a $^{28}$Si thin film deposited using this UHV ion source is shown in Fig.4(b). The average concentration level for carbon is $9.5(8) \times 10^{18}$ cm$^{-3}$; nitrogen is $5.5(5) \times 10^{18}$ cm$^{-3}$ and oxygen is $2.1(2) \times 10^{18}$ cm$^{-3}$ between 30 nm and 235 nm. As compared to the prior ion source, the total chemical purity of the $^{28}$Si film has been improved from $\approx 98.5$ % to 99.965(2) %. From previous SIMS measurement (not shown), we found that the $^{12}$C concentration in the film is roughly 400 times higher than $^{13}$C. This means that the $^{12}$C is also enriched (> 98.9 %) in the ion beam process and the $^{13}$C concentration is approximately $3 \times 10^{16}$ cm$^{-3}$. Similarly, the $^{15}$N concentration is < $2 \times 10^{16}$ cm$^{-3}$. Therefore, at this contamination level, the dominating factor for nuclear spin bath is still expected to be $^{29}$Si, plus some contributions from $^{13}$C and $^{15}$N as well. Future improvement in chemical purity is needed to reduce the effects from $^{13}$C and $^{15}$N.

Despite the substantial improvement in chemical purity (43x), we found the improvement was not fully correlated to the vacuum improvement (100x). This indicates that at this concentration level, the vacuum condition of the ion source is not the only limiting factor that affects the chemical purity of the $^{28}$Si film. We also found that the impurity concentrations are not correlated to the growth rate, indicating the origin of the impurities is from the ion source chamber instead of the growth chamber. Therefore, the cleanliness of the silane gas system (silane is highly reactive), impurity ions sputtering from the cathodes and anode materials and chemical compounds formed in the ion source plasma may be contributing factors. Further study is needed to fully explore the origin of the contaminations in the film and to seek additional purity improvements. Possible solutions may include reaching better ion source base pressure, using silane gas purifier to purify the gas line, and post-annealing at 950 °C in UHV (preliminary work shows that the N concentration can be reduced to low $10^{17}$ cm$^{-3}$ after annealing), etc. Electronic and quantum devices will then be developed to determine the deleterious impacts of the residual contaminants to relevant device performance.
**IV. Conclusion**

In this paper, we present the design, experimental implementation and performance of a UHV ion source system. The discharge properties based on arc voltage, source magnetic field and flow rate have been studied and optimized for $^{28}\text{Si}$. The performance of the UHV ion source for enriched silicon deposition is demonstrated through the ion mass spectrum and SIMS measurements of an enriched film. We show that the isotopically enriched $^{28}\text{Si}$ thin film deposited has high enrichment level of $99.99987(3)\% \left(\left(8.32 \pm 0.80\right) \times 10^{-7}\text{ mol/mol }^{29}\text{Si}\right)$ and chemical purity of $99.965(2)\%$, a substantial improvement over the prior ion source while maintaining the ability for highest enrichment among all methods reported. We believe this is an important step forward to produce high quality $^{28}\text{Si}$ that is suitable for quantum information studies.

**Tables**

TABLE I. Partial pressures of key gas contaminants relevant to silicon thin film purity as measured by residual gas analysis (RGA). Qualitatively the uncertainty is in the range of 10 % to 20 %.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Mass (u)</th>
<th>Pressure in prior ion source (Pa)</th>
<th>Pressure in UHV ion source (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>18</td>
<td>$&gt; 1.4 \times 10^{-7}$</td>
<td>$6.1 \times 10^{-10}$</td>
</tr>
<tr>
<td>$\text{N}_2$</td>
<td>28</td>
<td>$7.3 \times 10^{-8}$</td>
<td>$1.1 \times 10^{-9}$</td>
</tr>
<tr>
<td>$\text{O}_2$</td>
<td>32</td>
<td>$6.3 \times 10^{-8}$</td>
<td>$2.8 \times 10^{-11}$</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>44</td>
<td>$6.5 \times 10^{-8}$</td>
<td>$3.5 \times 10^{-10}$</td>
</tr>
</tbody>
</table>
Figures

Fig. 1. Simplified, cross sectional schematic diagram of the UHV ion source sliced along the axis—most parts are cylindrically symmetric. Insulating parts are shown in off-white. Consumable parts are dark red. The vacuum housing is unhatched with the stainless steel components shown in gray. The electromagnet solenoid is shown shaded brown and cross-hatched above and below the ion source insert. Source gas enters from the right, and ions are extracted to the left, where a system of electrostatic optics transports them downstream (not shown).
Fig. 2. $^{28}\text{Si}$ ion current (black) and discharge current (blue) characteristics: (a) as a function of arc voltage; (b) as a function of source magnetic field, and (c) as a function of SiH$_4$ flow rate. The measurement uncertainties are ± 1 nA for ion current and ± 0.2 mA for arc current, respectively.
Fig. 3. (a) The ion beam mass spectra of the prior (red dashed) and new (solid black) UHV ion source are shown for comparison. The ion current after passing through the mass selecting magnet shows six peaks, which consist mostly of $^{28}\text{Si}^+$ ions at 28 u and other isotopes combined with hydrides at higher masses. The peak shapes and isotope separation between 28 u and 29 u indicate similar enrichment capability. (b) A SIMS depth profile of $^{28}\text{Si}$ thin film shows the isotope fractions of $^{28}\text{Si}$, $^{29}\text{Si}$ and $^{30}\text{Si}$ using the UHV ion source, confirming excellent enrichment with an average of 99.99987(3) %.
Fig. 4. (a) Residual gas analysis (RGA) demonstrating the comparison in background gas density between the two ion sources. The red curve in (a) is the prior ion source with base pressure $2.7 \times 10^{-6}$ Pa ($2 \times 10^{-8}$ Torr) and the black curve is the UHV ion source with base pressure $2.7 \times 10^{-8}$ Pa ($2 \times 10^{-10}$ Torr). Major peaks are labeled with the dominant gases. (b) A SIMS depth profile of the residual chemical impurities in a $^{28}$Si thin film deposited using the UHV ion source. The estimated chemical purity of this sample is 99.965(2) %.

REFERENCES


