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Contract No: W911NF-18-1-0117

Project Title: Novel superconducting MgB2 nanowire-based qubits constructed by scanning tunneling microscope electron beam induced decomposition of newly developed CVD precursors

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Start Date: 04/01/2018
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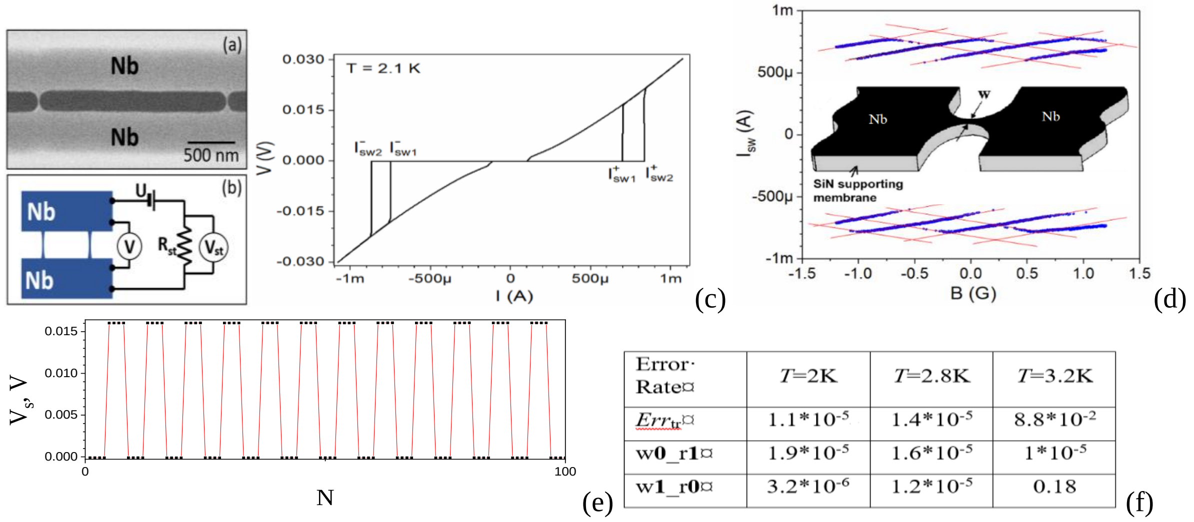
Nanowire qubit design (Bezryadin)

Our central goal was to develop a qubit design that would be compatible with the STM. We developed a prototype, which is a system of suspended SiN nanobridges connected to larger thin film electrodes (Fig.1a and Fig.1d (insert)). The system is compatible with STM. The key test outcomes are: (1) The system can be prepared in more than one quantized state, characterized by different values of the winding number, n, of the phase of the superconducting order parameter. (2) The vorticity n can be controlled with absolute precision by our current manipulation algorithm. (3) The vorticity n is very stable at temperatures below 2 K.

The sample (Fig.1a) consists of two nanobridges connected to thin (15 nm Nb) superconducting films (the "electrodes"). To fabricate the sample, a line-with-break pattern is prepared by e-beam lithography. The trench and nanobridges are etched in SF_6 plasma. Subsequent HF wet etching gives the undercut under the bridges. As the nanobridges are ready, a 15 nm Nb is sputtered over them and over the entire



Error·Rate¤	T=2K	T=2.8K	T=3.2K
Err_{tr}¤	$1.1*10^{-5}$	$1.4*10^{-5}$	$8.8*10^{-2}$
w0_r1¤	$1.9*10^{-5}$	$1.6*10^{-5}$	$1*10^{-5}$
w1_r0¤	$3.2*10^{-6}$	$1.2*10^{-5}$	0.18

(f)

Fig. 1. (a) Scanning electron micrograph of the sample. Two Nb bridges connect the top and the bottom Nb electrodes, separated by a 200 nm wide trench (black). (b) Measurement schematic. (c) The voltage-current curves measured over many cycles. (d) The multivalued critical current as a function of the perpendicular magnetic field B. T=2 K. (Insert) The insert shows the design of one of the Nb-coated SiN suspended bridges. (e) Testing the stability of the vorticity of the loop. The vorticity can be used to store information. (f) Results of extensive tests involving about 300000 write-and-read cycles.

substrate. Next, photolithography is used to select the nanowires and define the electrodes. The sample was measured at the temperature T=2 K. The results are summarized below.

The voltage-current (V-I) curve is shown in Fig.1c, measured as shown in Fig.1b. The bias current was cycled many times, so that the curve reveals two possible values of the critical current. They correspond to two different vorticity states as is revealed by the magnetic field bias effect on the critical current (Fig.1d). In order to create a definite vorticity state *n* we apply a bias current larger than the first critical current but lower than the second one. If the sample remain at zero voltage, then the state "zero" is created. If it switches to the normal state, then the bias current is reduced to zero and the procedure is repeated. As the state "zero" is created we read it out, also by measuring the critical current. Such write-and-read cycles were repeated many times (Fig.1e). The state with a definite *n* is stable. Thus, the rate of phase slips (thermal or quantum) is low, even at a relatively high temperature used in these tests. Finally, the system was tested as many as ~300000 times and the rate of various write-and-read errors turns out to be very low, of the order of 10^{-5}. Note that the absence of phase slips is a sign that if a similar system is used as a qubit it should not suffer from decoherence due to phase slips.

In the future we will use this technique to make MgB_2 and $Hf_{1-x}V_xB_2$ devices. These materials will be deposited in the Lyding lab and in the Girolami and Abelson labs. The samples will be tested in our microwave qubit setup. Etching the center of the nanobridge and depositing MgB_2 nanowires there should give us superconducting nanowire qubits.

Nanowire Writing (Lyding)

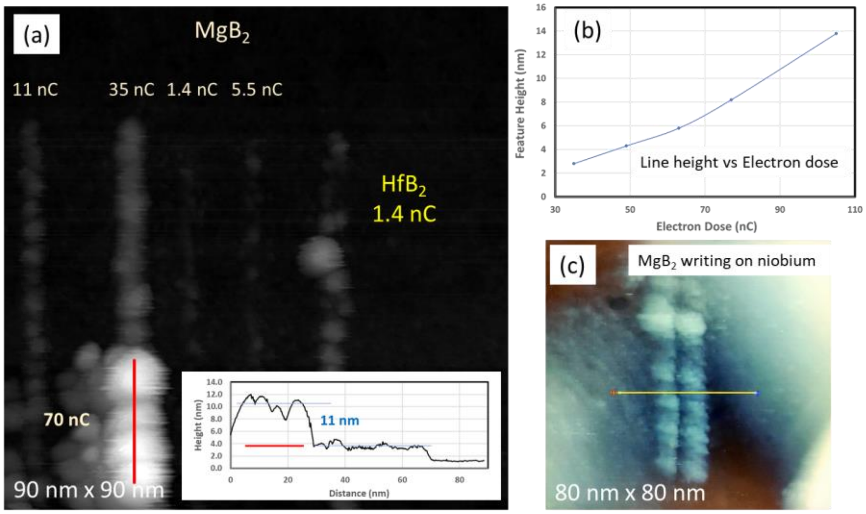


Fig. 2. (a) STM-written MgB_2 and HfB_2 lines on a silicon substrate, including a 11 nm high build-up placed at the end of one of the MgB_2 lines. (b) MgB_2 line height vs electron dose illustrating nucleation delay for doses below 60 nC. (c) MgB_2 line written on a niobium substrate. (Doublet is artifact of STM double-tip effect.)

The initial goal in this program was to develop a STM-based process for writing MgB_2 nanowires. This was successful, using the $Mg(DMADB)_2$ precursor fabricated by the Girolami group with results shown in Fig. 2 for nanowires written on both silicon and niobium substrates. Linewidths are in the desired sub-10nm range and STM spectroscopy indicates metallic behavior. Fig. 2b shows MgB_2 line height vs electron dose, illustrating a lower growth rate nucleation delay below 60 nC electron dose. At the end of this program writing was in progress on the trench samples produced by the Bezryadin group (see Fig. 3). Several issues having to do with lift-off and PMMA residue were worked on extensively, but these issues were not sufficiently resolved to produce a contacted nanowire in the UHV STM. Fig. 4 shows the status of this effort at the end of the project. Fig. 4a is a schematic diagram of a simple trench structure on an intrinsic silicon sample sized to fit on the STM sample holder. Fig. 4b is a

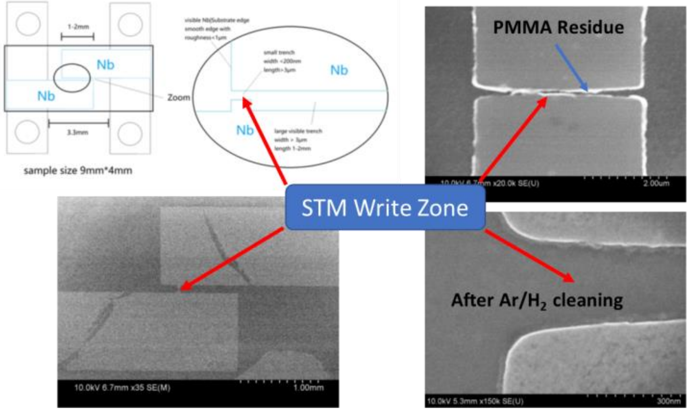


Fig. 3. Illustration and /SEM images of a two-Nb contact STM sample showing the 0.25 mm wide gap for nanowire writing. Also shown is the effect of Ar/H_2 annealing for removing PMMA residue.

UHV STM image of the trench region. Clearly evident are the 'dog ear' regions at the edges of the trench due to lift-off problems. A STM profile across the trench, Fig. 4c, shows that the dog ear regions are about 0.15 µm wide and range from about 5 nm to 20 nm in height. The niobium film thickness was 15 nm for this sample. The dog ear regions interfere with STM nanowire writing in two ways. First, STM tip convolution effects with the tall dog ear regions prevent the tip apex from reaching the true edge of the trench. Therefore, nanowires written in the trench will not contact the edges. Second, the dog ear material itself may interfere with good electrical contact to the underlying niobium layer.

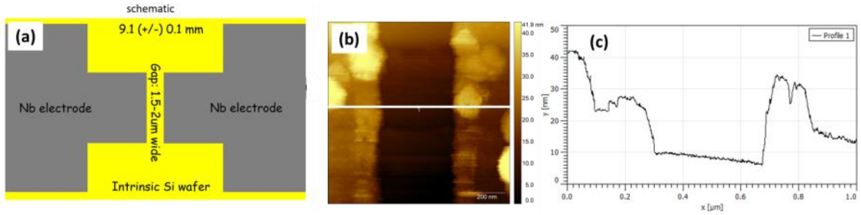


Fig. 4. (a) Schematic of trenched Nb sample sized for the STM sample holder. (b) STM image of the trench region. (c) STM height profile taken along the white line in (b), showing the trench and the dog ear regions at the trench edges.

In one case we were able to locate a dog ear-free region on one side of a trench and write a connected nanowire to that side. The result is shown in Fig. 5

While work continued in Bezryadin's group to resolve the dog ear problem, Lyding's group worked on two additional aspects of the overall fabrication process. One of these was to demonstrate that continuous nanowires could be written on the micron size scale of the trenches. Fig. 6 shows examples of long-length nanowire writing.

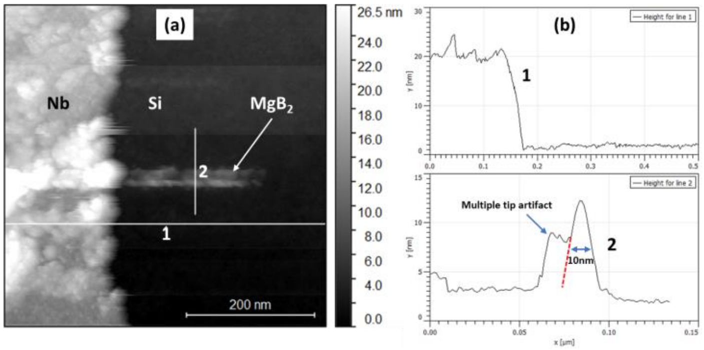


Fig. 5. (a) UHV STM image of a dog ear free region on one side of a trench with a MgB_2 nanowire written from the niobium contact into the trench. (b) Height profiles corresponding to the white lines in (a). The MgB_2 line appears artificially wide due to a STM tip shape convolution effect.

The other aspect of the overall fabrication was to encapsulate nanowire structures before removing them from the UHV STM system. MgB_2 is air sensitive, and its oxidation would be deleterious to potential superconducting properties. The method we used for this was to evaporate silicon from an intrinsic silicon sample under UHV conditions. Fig. 7 shows the SIMS analysis of the encapsulation process, indicating that the encapsulation layer is about 5nm thick.

Testing CVD Precursors (Abelson)

The goals of this part of the program were to (i) test novel molecular precursors developed by Girolami that are intended for STM direct-write of superconducting lines; and (ii) to develop large-area deposition of superconducting films by thermal CVD, which will afford superconducting pads and interconnects in the Qbit device design.

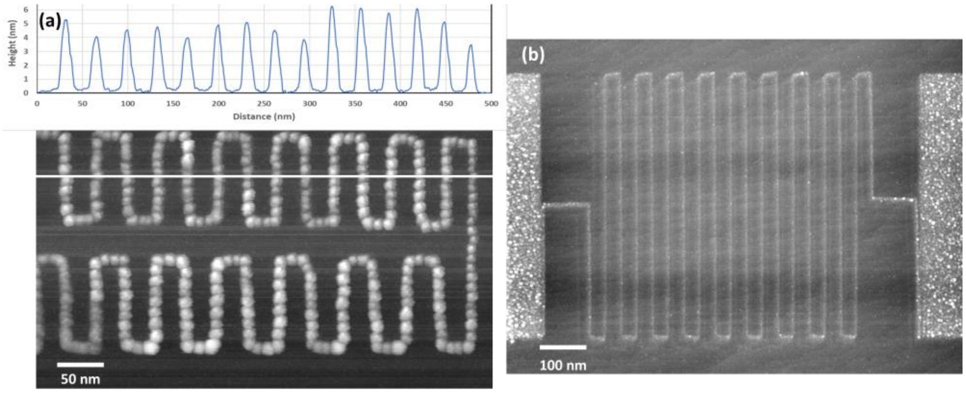


Fig. 6. Demonstrations of long-length continuous MgB_2 nanowire writing. (a) Serpentine nanowire written across a 0.5 mm field width, with a line profile demonstrating ~5 nm nanowire height. (b) Serpentine nanowire written across a 1 μm field with high-density ends to promote electrical contacting.

Results

Precursor $Mg(DMADB)_2$. MgB_2 must be grown at substrate temperature < 400°C to avoid Mg evaporation from the film and loss of superconductivity. The $Mg(DMADB)_2$ precursor has high vapor pressure but CVD appears not to proceed below 400°C. In prior work we discovered that low-temperature CVD can be catalyzed by co-flow of a second precursor that affords a MgB_2 compound, such as HfB_2, ZrB_2 or TiB_2.

A deposition protocol based on the addition of $Ti(DMADB)_2$, which is the direct analogue of the Mg precursor (same ligands). The resulting $Mg_{(1-x)}Ti_xB_2$ films contain an excess of oxygen which impedes formation of crystalline material; as of this writing, the source of oxygen has been identified and is being eliminated. A concern is that Ti, which is present in alloy concentrations $x \sim 0.2$, introduces too many electrons which will degrade superconductivity.

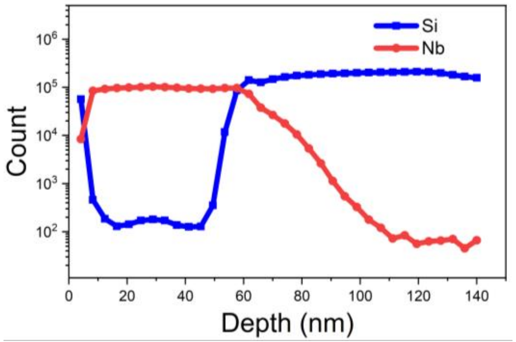


Fig. 7. SIMS profile showing a 5 nm thick Si encapsulation layer deposited in the UHV STM system on a Nb/Si substrate. The encapsulation is shown by the rise in the Si content at <10 nm depth.

Precursor $Mg(NBNB)_2$. Preliminary experiments show that CVD of MgB_2 can proceed using this newly-synthesized precursor.

Precursor development (Girolami)

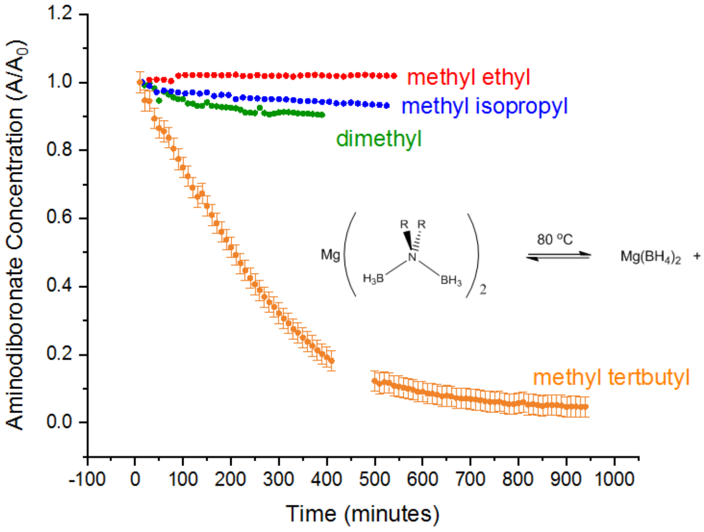


Fig. 8. Comparison of the thermal stability of magnesium aminodiboranates with different alkyl groups on nitrogen.

One of the goals of the Girolami group is to make improved molecular precursors for the STM direct writing of MgB_2 nanowires as the superconducting component of a qubit device. To achieve this goal, the Girolami group investigated the synthesis of previously-unknown magnesium compounds bearing *N*,*N*-dialkylaminodiboranate groups, $(BH_3)_2NRR'$, where R and R′ are alkyl groups. The compound with R = R′ = methyl has the highest vapor pressure of any known magnesium compound (800 mTorr at room temperature) but is thermally very stable. In the 2019-2020 project year, they completed the synthesis of five new magnesium aminodiboranate compounds with sterically larger R and R′ groups, with the expectation that the increased steric bulk would reduce the N-B bond strength, lower the thermal stability of the Mg compounds, and lead to improvements in the STM direct writing process for making MgB_2 nanowires.

Of the five new magnesium compounds the Girolami group made, most have thermal stabilities that are similar to that of the parent compound with R = R′ = methyl. One of the new compounds, however, behaves very differently: the compound with R = methyl and R′ = tert-butyl (a very large substituent) is much more thermally reactive (Fig. 8). It undergoes more extensive B-N bond cleavage than precursors with smaller R groups. This compound is targeted for STM direct write studies of MgB_2 in the next grant year.

A second goal of the Girolami group was to prepare vanadium compounds that can serve as precursors (along with hafnium borohydride) for the STM direct write of wires of a different superconductor, vanadium-doped hafnium diboride, $Hf_{1-x}V_xB_2$, which has a T_C of 8 K at 4% doping. At the beginning of the project, no volatile vanadium borohydride compounds were known. In the 2019-2020 grant year, the Girolami group was successful in synthesizing the first such compound: it has the stoichiometry $V(NMe_2BH_2NMe_2BH_3)_2$ (Fig. 9). This compound is the first volatile vanadium borohydride complex to be discovered: it sublimes readily at 20 °C under moderate vacuum. Samples of this compound were made available to the Abelson and Lyding groups to investigate using it to make superconducting vanadium-doped HfB_2.

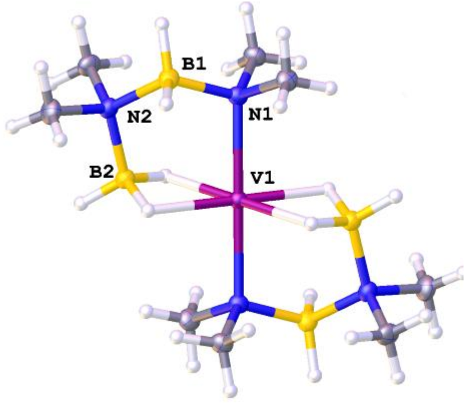


Fig. 9. Molecular structure of $V(NMe_2BH_2NMe_2BH_3)_2$.

Publications and Dissemination:

The following is a list of the published work, in preparation for publication work, and major presentations resulting from this program:

Supercurrent-controlled kinetic inductance superconducting memory element
E Ilin, X Song, I Burkova, A Silge, Z Guo, K Ilin, A Bezryadin
Applied Physics Letters 118, 112603 (2021).

C. M. Caroff, B. J. Bellott, C. I. Daly, S. R. Daly, A. C. Dunbar, J. L. Mallek, M. A. Nesbit, and G. S. Girolami, "Sodium Aminodiboranates Na(H3BNR2BH3). Structural and Spectroscopic Studies of Steric and Electronic Substituent Effects" submitted for publication.

L. Souqui, C. M. Caroff, G. S. Girolami, and J. R. Abelson, "CVD of MgH_2 Thin Films using Magnesium Bis-diamidodiboranate" in preparation for publication.

P-C. Huang, H. Sun, M. Sarker, C. M. Caroff, G. S. Girolami, A. Sinitskii, and J. W. Lyding, "Precise Metal Contact on a Single Atomically Precise Graphene Nanoribbon with Sub-5 nm Metallic Hafnium Diboride Nanostructures" in preparation for publication.

J. W. Lyding, "Nanofabrication on Silicon: Transitions to Technology" Invited Talk, International Association of Advanced Materials Lecture Series, May 18, 2021.

J. W. Lyding, "Silicon-Based Nanofabrication and Transitions to Technology" Invited Seminar, UT Dallas Quantum Seminar Series, April 15, 2021.

Honors:

Joseph W. Lyding received the International Association of Advanced Materials Medal with the citation "In recognition for his contribution to Nanomaterials Synthesis", 2021.