Development of nano and micro SQUIDs based on Al tunnel junctions

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Abstract. Superconducting quantum interference devices (SQUIDs) with nano (micro)-meter dimensions are called nano (micro)-SQUIDs. The high sensitivity for flux and position of nano (micro)-SQUIDs can be applied to detect local magnetic fields induced by vortices and the magnetization of mesoscopic superconductors. Nano-SQUIDs based on carbon-nanotube junctions and niobium weak junctions are well known. However, such nano-SQUIDs are not suitable for large-scale integrated circuits and mass production. Therefore, we employ a combination of lithography using the Niemeyer-Dolan technique and the inductively coupled plasma reactive-ion etching technique to fabricate nano-SQUIDs. Here, we report the fabrication of nano (micro)-SQUIDs based on superconducting aluminum tunnel junctions and their application for vortex formation into mesoscopic chiral superconducting Sr$_2$RuO$_4$ [1-3].

1. Introduction
Superconducting quantum interference devices (SQUIDs) are used as sensitive magnetometers in a wide range of fields. Recently, nanometer-sized SQUIDs (nano-SQUIDs) have attracted considerable attention because of their high resistance to external flux noise and their ability to detect magnetic fields induced by a single electron spin [4-9]. Nano-SQUIDs also play an important role in quantum computing...
as a quantum interface between spin qubits and SQUID-based superconducting qubits [10-15]. Nano-SQUIDs have a high sensitivity not only in the flux but also in the position. The smallest resolution of a sensor is finally determined by the size of the probe. Therefore, the nano-SQUID is applied to the scanning probe microscopy [16-18].

There are well-known nano-SQUIDs based on carbon nanotube junctions or weak-link junctions consisting of niobium [4, 7-9, 19]. However, such nano-SQUIDs are not suitable for large-scale integrated circuit fabrication, such as a quantum computing circuit or a sensor based on the SQUID array, because they must be fabricated one by one. Moreover, it is not easy to suppress the critical current of the weak-link junction. In order to realize a nano-SQUID with well-controlled Josephson junctions and high integration for such as a nano-SQUID array, we employ a combination of lithography using the Niemeyer-Dolan technique[20, 21] and the inductively coupled plasma reactive-ion etching technique (ICP-RIE)[22]. We developed a new fabrication process applicable for nano-SQUIDs comprising a superconducting aluminum loop and high-quality superconducting tunnel junctions, which are applicable to superconducting qubits[13, 14].

Dolan-bridge shadow deposition is a standard method to realize superconducting small-tunnel junctions containing superconducting qubits. However, tilted deposition undesirably broadens the width of the superconducting electrodes. That is, vortices are trapped in the wide superconducting electrodes in the magnetization measurement. By performing the RIE, it is possible to narrow the width of the electrodes independently of the shadow deposition.

In this paper, we report our work on the fabrication of micro- and nano-SQUIDs based on superconducting aluminum tunnel junctions. To fabricate the SQUIDs with aluminum tunnel junctions, we employ a combination of the Dolan bridge shadow evaporation technique [20] and the ICP-RIE method.

2. Experimental methods

Our lithography process for SQUIDs is separated into three parts. First, we fabricate the large structures: the bonding pads, Au electrodes, and registration marks for the subsequent e-beam lithography. The optical lithography for the large structures is performed in two separate processes to prevent step-disconnection between the Au electrodes and Al SQUID electrodes and to assure the sufficient film thickness for the wire bonding and registration mark for the electron beam lithography.

After suitably cleaning a silicon wafer, a common primer HMDS is used before a spin-coating of resists that serves as an adhesion promoter. Subsequently, the bilayer resist is spun on. To produce the bilayer resist, the LOR5A polydimethylglutarimide is first spin-coated onto the wafer at 3000 rpm for 60 s after the ramp up for 10 sec and soft baked to drive out the solvent at ~180 °C for 5 min. Next, the AZ5214E copolymer is spin coated in the same manner onto the coated LOR5A film and soft baked at ~110 °C for 2 min. This results in each layer being approximately 550 or 1620 nm thick for a total film thickness of approximately 2120 nm. Then, we use direct laser writing to expose the patterns for the electrical leads with a dosage of 140 mJ/cm$^2$ using a maskless disposer system that is manufactured by Nanosystem Solutions, Inc. The exposed wafer is developed in 2.38% TMAH (tetramethylammonium hydroxide) for 90 sec to remove the exposed AZ5214E and LOR5A, leaving windows in AZ5214E/LOR5A bilayer for the electrodes. Subsequently, the developed sample is rinsed by deionized (DI) water for 30 sec.

After the photolithography and development of the structure, a first metal layer of Ti/Au is deposited by electron beam physical evaporation in a high-vacuum chamber with a base pressure of a few 10$^{-6}$ Pa. The first deposition of Ti 5-nm and Au 50-nm films on the surface of the sample was performed under a pressure of a few 10$^{-5}$ Pa. After the metal deposition, liftoff is performed to remove all of the unwanted metal and resist polymers. Liftoff is achieved by soaking the metal-coated sample in NMP (N-methylpyrrolidone) for at most 40 min, at 80 °C. After the liftoff, the sample is rinsed with acetone for 30 s and then isopropanol (IPA) for 30 s and finally dried by nitrogen gas. In the 2nd process for the 2$^\text{nd}$
Ti/Au layer, the lithography process is performed in same manner as for the 1st Ti/Au layer, but the thickness of the deposition differs between the Ti 50-nm and Au 200-nm films.

Next, smaller SQUID electrodes are fabricated by electron beam lithography. The bilayer resist is spun on to make a structure for the shadow deposition method. To produce the bilayer resist, the PMGI SF7 polydimethylglutarimide, which is a highly soluble polymer covering with a thin layer of the actual e-beam resist, is first spin coated onto the wafer at 3000 rpm for 60 sec after the ramp up for 10 sec and then soft baked to drive out the solvent at ~180 °C for 5 min. Next, the high-resolution electron beam resist ZEP520A is spin coated onto the coated PMGI SF7 film and soft baked in the same manner. This results in each layer being approximately 600 or 100 nm thick, for a total film thickness of approximately 700 nm. We then use an electron beam to expose the patterns for the SQUIDs electrodes. Then, the wafer is cut to several chips to make tunnel junctions with different parameters. Since the degradation of the pattern starts after the development, the deposition must be done immediately. However, the exposed sample without development can be preserve for several months. The chips are developed twice first in Xylene for 30 s to dissolve the exposed ZEP520A and rinsed in IPA for 30 s, then in 2.38% TMAH for 22 s to dissolve portions of PMGI SF7 via the ZEP520A windows and rinsed by DI water for 30 s.

After e-beam lithography and development of the SQUID structure, we perform the shadow evaporation method, which was proposed by G. J. Dolan in 1977, to form the tunnel junction [20, 21]. First, a 30-nm-thick aluminum layer is deposited on the angle of plus ten degrees by electron beam physical evaporation in a high-vacuum chamber with a base pressure of a few 10⁻⁶ Pa.

After the first Al film deposition, the oxidation of the first deposition Al surface was performed in a sub-chamber for forming an insulating film for the tunnel junctions. The sample can be transported from the main chamber to the sub chamber without breaking the vacuum. The oxidation is controlled by the oxygen flow rate, pressure, and time. As a result, the critical current density $J_c$ of the JJs is easily adjustable. Subsequently, a 2nd 50-nm-thick Al film is deposited in the main chamber on the angle of minus 10 degrees.

To realize a smooth surface of Al, it is important to fabricate a film that is uniform, thin, and a good insulator. When the Al is placed directly into a cold copper hearth, because of the high thermal conductivity of the aluminum and cooper, the evaporation rate is very low. Therefore, a boron nitride hearth liner is used to satisfy the deposition rate. The surface of the deposition aluminum film obtained using the boron nitride hearth liner is smoother and has a smaller grain size than that obtained using the alumina hearth liner.

Fabrication of micrometer-sized SQUIDs is finished by the previous process. However, to make nanosQUIDs, we add an extra process using ICP-RIE. For the etching mask of the ICP-RIE, e-beam lithography is performed using a single-layer resist of the ZEP520A. The spin coating, baking, and exposing are done in the same manner as in the SQUID lithography process. After the development of the exposed ZEP520A, dry etching was performed using a Cl₂ and BCl₃ ICP-RIE process for 2 min with powers of 50 W ICP and 150 W, respectively. Cl₂ gas is suitable for etching metal such as aluminum; however, it is not suitable for etching Al₂O₃. In our structure, there are two Al₂O₃ films: one is the native oxide film on the surface, whose thickness is ordinary expected to be approximately 4 nm, and another is the film for the tunnel junction, whose thickness is expected to be 1 nm. BCl₃ gas is widely used for the etching of materials covered by native oxides owing to its effective extraction of oxygen [22, 23]. Therefore, we chose a mixture gas of Cl₂ and BCl₃ for the etching which is also widely used for the etching of thin metal films with native oxide. The etchant gases of Cl₂ and BCl₃ are introduced into the chamber at 8 and 2 sccm, respectively. The total pressure is controlled at 0.1 Pa.

Figure 1 (c) shows a scanning electron microscopic image of the fabricated nano-SQUID. The width of the electrodes of the nano-SQUID is 100 nm, which is twice the Meissner length of superconducting aluminum at zero temperature. The inner area of the nano-SQUID is 500 × 500 nm².

For setting the microscopic size samples onto the micro- and nano-SQUIDs, we typically use a nano-manipulator system that is manufactured by Omniprobe Inc., primarily for transmission electron microscope (TEM) sample preparation. During transportation, the sample was attached to the tip of a
small tungsten needle. The accuracy of the setting position was approximately 100 nm, and the minimum size of the sample for the transportation was approximately 1 μm. To reduce the size to below 1 μm, the sample need to be milled by using focused ion beam on the nano-SQUIDs. Figure 1 (d) shows a scanning electron microscopic image of the micro-SQUID with a mesoscopic plate of the chiral superconductor Sr₂RuO₄ [1-3].

For measurement, a dilution refrigerator with a base temperature of 30 mK or helium 3 refrigerator with a base temperature of 300 mK is used for cooling the sample to below the critical temperature of aluminum, which is $T_c = 1.2$ K. Because the small critical current of the Josephson junction is very sensitive to environmental noise, the supercurrent readily disappears. Therefore, a 0.1-μF chip ceramic capacitor for filtering is mounted between the measurement line and electrical ground nearby the sample, and a copper powder filter is installed at the mixing chamber stage in the dilution refrigerator [24].

3. Results and discussion

Figure 1. (a) Typical $I$-$V$ characteristics of nano-SQUID at $\sim 75$ mK in the absence of a magnetic field. (b) Field dependence of the critical current of nano-SQUID. (c) Scanning electron microscopic image of a nano-SQUID. Red circles show the position of SIS Josephson junctions. Yellow lines show the edge of Al electrodes of SQUID. There are residual outside of the electrodes, however these are insulated. (d) Mesoscopic plate of the chiral superconductor Sr₂RuO₄ is set onto corner of the left micro SQUID using nano-manipulator system.

Figure 1 (a) shows a typical $I$-$V$ characteristic of nano-SQUID at $\sim 75$ mK in zero magnetic field. The duration of a bias current cycle is typically 1 s. The $I$-$V$ characteristic indicates a clear supercurrent with the critical value of $I_c$ below 1 μA with hysteretic behavior. As a function of an external field, a periodic oscillation of the critical current $I_c$ is observed, as shown in Fig. 1(b). The critical current is defined at
switching currents between the superconducting state and the voltage state in the \( I-V \) curves. The observed period of approximately 6.6 mT is consistent with the addition of a flux quantum \( \Phi_0 = \hbar/2e \) to the effective SQUID area of 550 nm \( \times \) 550 nm.

4. Conclusions
We developed a fabrication process for nano (micro)-SQUIDs based on superconducting aluminum tunnel junctions. The critical current is sufficiently small to avoid a heating at switching to the voltage state. The field dependence of the critical current shows typical behaviors of SQUIDs. In the future, we will apply this process to make SQUID arrays for the measurements of vortex formations in microscopic superconducting plates.

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References
[1] Y. Maeno, S. Kittaka, T. Nomura, S. Yonezawa, and K. Ishida, J Phys Soc Jpn 81, 011009 (2012).
[2] Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz, and F. Lichtenberg, Nature 372, 532 (1994).
[3] A. P. Mackenzie and Y. Maeno, Rev Mod Phys 75, 657 (2003).
[4] S. K. H. Lam and D. L. Tilbrook, Applied Physics Letters 82, 1078 (2003).
[5] V. Bouchiat, Superconductor Science & Technology 22 (2009).
[6] C. Granata, A. Vettoliere, P. Walke, C. Nappi, and M. Russo, Journal of Applied Physics 106 (2009).
[7] A. Vettoliere, C. Granata, E. Esposito, R. Russo, L. Petti, B. Ruggiero, and M. Russo, Ieee T Appl Supercon 19, 702 (2009).
[8] W. Wernsdorfer, Superconductor Science & Technology 22 (2009).
[9] L. Bogani, R. Maurand, L. Marty, C. Sanggregorio, C. Altavilla, and W. Wernsdorfer, J Mater Chem 20, 2099 (2010).
[10] O. Buisson et al., Quantum Information Processing 8, 155 (2009).
[11] S. Kim, R. Ishiguro, M. Kamio, Y. Doda, E. Watanabe, D. Tsuya, K. Shibata, K. Hirakawa, and H. Takayanagi, Applied Physics Letters 98, 063106 (2011).
[12] S. Kim et al., AIP Conf. Proc., 383 (2011).
[13] G. Blatter, V. B. Geshkenbein, A. L. Fauchere, M. V. Feigel'man, and L. B. Ioffe, Physica C 352, 105 (2001).
[14] H. Takayanagi, H. Tanaka, S. Saito, and H. Nakano, Physica Scripta T102, 95 (2002).
[15] F. Plastina and G. Falci, Physical Review B 67 (2003).
[16] D. Vasyukov et al., Nature nanotechnology 8, 639 (2013).
[17] A. Finkler et al., Nano Lett 10, 1046 (2010).
[18] J. Nagel et al., Physical Review B 88 (2013).
[19] J. P. Cleuziou, W. Wernsdorfer, V. Bouchiat, T. Ondarcuhu, and M. Monthioux, Nature nanotechnology 1, 53 (2006).
[20] G. J. Dolan, Applied Physics Letters 31, 337 (1977).
[21] J. Niemeyer and V. Kose, Applied Physics Letters 29, 380 (1976).
[22] J. R. Rooth, *Industrial Plasma Engineering* (Taylor & Francis Philadelphia, 1995), Vol. 1.
[23] G. M. Xue, H. F. Yu, Y. Tian, H. Deng, W. Y. Liu, Y. F. Ren, H. W. Yu, D. N. Zheng, and S. P. Zhao, Sci China Phys Mech 56, 2377 (2013).
[24] A. Lukashenko and A. V. Ustinov, Review of Scientific Instruments 79 (2008).