A multilayer, high resolution, ion-bombardment-tolerant electron resist system

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(Received 11 June 1981; accepted 14 August 1981)

A multilayer, high resolution electron resist system, which withstands ion bombardment, has been developed. This system consists of four layers which are, from top to bottom: AZ1350B, a thin metal interlayer, PMMA, and a copolymer of PMMA. The bottom two layers define the actual pattern dimensions. Two independent developers have been chosen for these two layers in order to obtain controllably undercut resist profiles ideal for liftoff applications, while maintaining high resolution in the upper PMMA layer. The top two layers of the four-level system serve to provide a protective metal coating which prevents crosslinking of the underlying polymer layer. This allows processing involving ion bombardment, such as ion milling or reactive ion etching. Without this protective metal layer, difficulty is often encountered in liftoff processing after ion bombardment, due to the presence of a thin crosslinked polymer layer which resists solvent penetration. This resist system has been used in conjunction with reactive ion beam oxidation to fabricate high quality, small area, niobium–lead alloy tunnel junctions in an edge geometry. Using a standard Cambridge EBMF-2 microfabricator, junctions with linewidths as small as 0.25 μm have been produced. With the edge geometry, this corresponds to junction areas smaller than 4 × 10^-10 cm².

PACS numbers: 81.60.Jw, 61.80.Jh, 74.50. + r, 85.30.Mn

Thin film device fabrication often involves the cleaning or dry etching of one material with the subsequent deposition and patterning of a second material over the cleaned area. In order to prevent reoxidation or recontamination of the surface of the freshly cleaned layer, it is desirable to clean and deposit in the same high vacuum system. Thus vacuum-compatible methods of cleaning such as reactive ion etching or ion beam etching must be used. Patterning of the deposited layer by standard liftoff techniques is then possible, provided the resist stencil is durable enough to withstand the cleaning process without significant erosion or distortion, while remaining soluble in the liftoff solvent. Polymeric resist materials, such as PMMA, often fail to meet these requirements because of their poor dry etch resistance and their tendency to crosslink under ion bombardment.

This paper describes a multilayer, high resolution, electron resist system which minimizes crosslinking and resist erosion during ion bombardment processing. This system also provides reproducibly undercut profiles well suited to the liftoff of thick deposited layers. After presenting the details of the multilayer resist system, the fabrication of small area, high current density Nb–PbBi Josephson tunnel junctions will be described to demonstrate its capabilities.

The electron resist system consists of four layers as illustrated in Fig. 1. These layers are from top to bottom (with typical thicknesses): 0.2 μm of AZ1350B; 500 Å of Al; 0.2 μm of PMMA; and 0.5 μm of a copolymer of methyl methacrylate and methacrylic acid. The percentage of methacrylic acid is 8.5%. The top two layers of this system provide protection from ion bombardment, while the bottom two layers form a bilayer resist system which can be used alone if no ion cleaning is needed during device processing. Since this system can be used independently of the top two layers for high resolution liftoff processing, it will be described in detail before we discuss the complete four layer system.

The bilayer resist system is similar to a system described by Howard et al. and is also based on the work of Hatzakis. The thick copolymer layer in the two level system acts as an offset layer. It planarizes substrate topography and minimizes backscattering at the top layer since it is a relatively low Z material. High resolution is obtained in the top PMMA layer due to the low level of backscattering and the

![FIG. 1. Four layer resist system. (a) Electron beam exposure of composite system. (b) Development of the top layer and etching of the Al layer. (c) PMMA development. (d) Copolymer development to produce undercut.](image-url)
thinnness of the layer. With the proper choice of developing solvents, the differing polar characteristics of these two polymers allows one to obtain controllably undercut profiles suitable for liftoff. Because the copolymer is more polar in character than PMMA, it is possible to produce undercut profiles using a single relatively polar solvent as a developer for the bilevel system. However, in this case there is a competition between resolution and undercut because the top layer continues to be weakly attacked as the bottom layer is developed. This competition can be avoided by developing the PMMA and the copolymer in mutually exclusive solvents. The following two combinations of solvents are found to work well as top and bottom layer developers: the PMMA is developed in a 1:3 mixture of toluene to isopropyl alcohol for 15 to 25 s, and the copolymer is developed in a 1:5 mixture of ethyl cellosolve acetate (ECA) to ethanol for 45 to 75 s. This choice of developers allows independent development of the two layers so that undercut can be adjusted freely without affecting resolution in the top layer. Figure 2 shows typical resist profiles obtained with the bilayer, two-developer system. These lines were exposed with a standard Cambridge EBMF-2 at a line dose of about $3.0 \times 10^{-9}$ C/cm. The substrate is Si coated with 0.2 μm of Nb (to simulate Josephson tunnel junction fabrication conditions) and the linewidths are about 0.25 μm. Linewidths as small as 0.15 μm have been produced with the limitation being the spot size of the EBMF-2 electron beam, not the resolution of the resist.

Although the bilevel, two-developer system is suitable for many applications, we have found that this system must be modified if ion beam cleaning is used before liftoff. The modification is necessary because the ion bombardment encountered during a typical cleaning process causes substantial crosslinking in the PMMA. Without the crosslinked layer, liftoff occurs readily, but when the crosslinked layer is present liftoff is very rarely possible. Apparently the crosslinked layer resists solvent penetration much more effectively than a deposited metal layer, and sideways penetration of the solvent is not effective. This problem could possibly be avoided by modifying the chemical structure of the polymer to make it less susceptible to crosslinking. We chose, however, to use unmodified PMMA because of its proven very high resolution capabilities. Given this choice, one can either prevent ion from entering the resist through the use of a suitable noncrosslinking mask above the polymer layer, or one can vary the ion cleaning parameters in the hope of reducing the ion dose received by the PMMA. The following analysis shows, however, that in general it is not possible to reduce the ion dose below the crosslinking threshold by

FIG. 2. Typical resist profiles in PMMA–copolymer bilevel system.
varying ion bombardment parameters, while maintaining effective cleaning.

For concreteness we consider the case of ion beam cleaning with a Kaufman type ion source, using as an example typical beam parameters suitable for removing approximately 100 Å of niobium and niobium oxide. The parameters are: beam current density ($J$) = 0.125 mA/cm²; accelerating voltage ($V_a$) = 600 V; milling time ($t$) = 10 min. The range of 600 eV Ar ions in PMMA is only about 50 Å so that the crosslinked layer remaining after milling is extremely thin. Its effective thickness may be as large as several hundred Å, though, due to the length of the polymer chains in our high molecular weight PMMA (M.W. ≥950 000). The ion dose received by the PMMA surface can be calculated if one accounts for the fact that the polymer is being eroded away as it is being bombarded. The total dose received by the final PMMA surface remaining after the ion mill cleaning is terminated is given by

$$D = JT = \frac{JR}{r},$$

where $J$ is the beam current density, $T$ is the time taken to mill a distance $R$, $R$ is the range of the ions striking the resist, and $r$ is the milling rate of the resist ($r$ ≥ 50 Å/min for

FIG. 3. Edge junction fabrication process. (a) An Al₂O₃ layer acts as an ion mill mask for the Nb film. (b) A faceted edge is left after milling. (c) After evaporation of the counterelectrode, a junction is formed on the edge. (d) Junction dimensions are determined by Nb thickness and overlap linewidth.

FIG. 4. SEM micrograph of a Nb-PbBi tunnel junction fabricated using the four layer resist system.
PMMA in this case). Substituting the typical parameters listed above gives \( D \approx 5 \times 10^{16} \text{ Ar ions/cm}^2 \). Since the 600 eV Ar ions travel 50 Å, their average energy dissipation is 120 eV/nm and at this dissipation rate the critical dose needed to crosslink PMMA is \( D_c \approx 4 \times 10^{14} \text{ Ar ions/cm}^2 \). Thus we are two orders of magnitude above the crosslinking threshold. Furthermore, it is known that (1) the ion range, \( R \), is proportional to the ratio of the ion energy to the ion atomic number\(^{12}\); (2) the milling rate, \( r \), is roughly proportional to the ion energy in the energy range of most ion mills\(^{13}\); and (3) sputtering yields are roughly constant for inert gas ions in this energy range.\(^{14}\) Therefore the ion dose \( D \) is proportional only to the inverse of the ion atomic number. Thus using Xenon ions for milling rather than Ar ions would decrease the dose to a third of its original value. This, however, still leaves us well within the crosslinking regime and an alternate solution must be implemented.

The solution proposed in this paper is to pattern a thin metal layer over the PMMA to prevent ions from ever entering the resist, thereby eliminating crosslinking. Figure 1 shows how this is accomplished. A 500 Å layer of aluminum is evaporated over the bilayer copolymer-PMMA system and 0.2 μ of AZ1350B is spun on over that. The composite structure is then exposed with an electron beam in the same manner as the two-layer system. After exposure the AZ1350B is developed in a 1:5 mixture of AZ2401 to water. The aluminum is then etched in a mixture of phosphoric and nitric acids and water, followed by a brief rinse in the basic 1:5 AZ2401-water solution. The basic rinse is necessary for proper development of the PMMA. Finally the bottom two resist layers are developed in the same manner as described previously. The solvents used for development of these layers also dissolve away the AZ1350B. This development process results in an undercut, high resolution stencil which is covered by a protective layer of aluminum. The metal layer mills relatively slowly and stops Ar ions before they penetrate the PMMA. Thus crosslinking is prevented and the etch resistance of the resist system is improved. Aluminum has been chosen here because it is conveniently evaporated and etched, but different metals can be substituted for the Al layer if improved etch resistance to a particular reactive etching gas is desired, for example. Also note that the Al is typically etched back slightly from the opening in the PMMA stencil due to the higher electron sensitivity of the AZ1350B layer and hence the wider linewidth that layer. This presents no problem for normal ion cleaning processes because so little material is removed, but if a significant amount of material must be etched the protective metal layer

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**FIG. 5.** Typical I–V characteristic of a Nb–PbBi tunnel junction. The vertical and horizontal scales are 10 μA/div and 1 mv/div.
should extend to the edge of the PMMA stencil. This can be accomplished by using a slightly modified resist system and development scheme. In this case, PMMA replaces AZ1350B as the uppermost layer. After exposure the top PMMA layer is developed and the metal interlayer is chemically or reactively ion etched. Next an oxygen ion etch is used to remove the top PMMA layer so that it cannot crosslink under ion bombardment, and at the same time transfer the pattern through the metal stencil to the lower PMMA layer. Finally, an undercut profile is produced by developing the copolymer layer in the same manner as before.

When using either of these resist systems for ion cleaning and liftoff applications, one other processing step should be added for optimum results. We have found that although the undercut resist walls are not directly exposed to the ion beam, sufficient ions scatter off the substrate to strike and crosslink these walls. The crosslinked walls can often be removed in the ultrasonic cleaner during the liftoff process, but they sometimes remain. A more reliable means of eliminating the resist walls is to use an oxygen plasma etch either before or after liftoff.

This resist system was originally developed during our efforts to fabricate very small area, high current density Nb-PbBi Josephson tunnel junctions. Small junction areas (10^{-9} to 10^{-10} cm^2) are necessary to obtain Josephson devices possessing both very high frequency response (\sim 1 THz) and useful impedance values (\sim 50 \Omega). The key to our fabrication scheme is to minimize junction area by using an edge geometry to confine one dimension of the junction and electron beam lithography to confine the other dimension. The fabrication process is illustrated in Fig. 3. A photolithographically defined Al_{2}O_{3} layer is used as an ion milling mask to cut an edge in an Nb film. Next, the four-level resist system (Fig. 1) is applied over the edge. A counterelectrode pattern is exposed in the resist and developed as described previously. The Nb edge exposed by the resist stencil is cleaned using an Ar ion beam and then oxidized using an Ar/O_2 ion beam. Finally, a PbBi counterelectrode is evaporated and lifted off. Notice that the junction dimensions are determined by the thickness of the Nb film and the width of the e-beam defined counterelectrode tip. The four-level resist system provides good coverage of the Nb edge while retaining high resolution capabilities in the offset PMMA layer. The liftoff of the PbBi counterelectrode is reliable and easy despite the Ar ion cleaning process, because of the protective Al layer and the undercut resist profile. Using this fabrication scheme and a standard Cambridge EBMP-2 microfabricator we have made tunnel junctions with counterelectrode tips as small as 0.25 \mu m. With the edge geometry this corresponds to junction areas smaller than 4 \times 10^{-10} cm^2. A scanning electron micrograph of one such junction is shown in Fig. 4 and a typical I-V characteristic appears in Fig. 5. The response of these devices at very high frequencies is currently being investigated using a far infrared laser as a radiation source in 4THz range.

Acknowledgments: This research was supported by the NSF through the National Research and Resource Facility for Submicron Structures at Cornell University.

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6The copolymer is commercially available from Esschem Co., Essington, PA.