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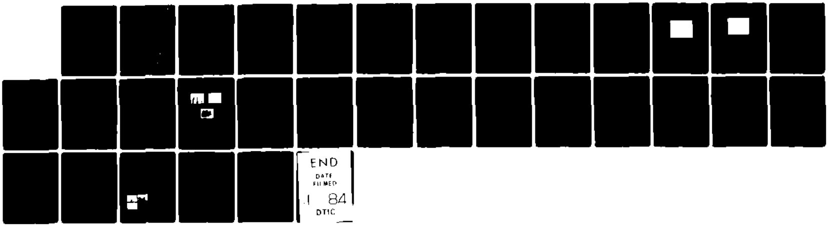

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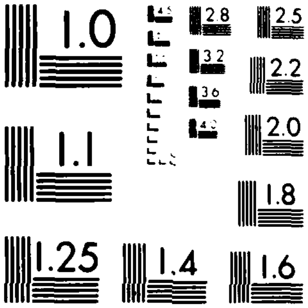
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TUNNELING THROUGH AMORPHOUS SILICON BARRIERS

H. Kroger, L. N. Smith, D. W. Jillie and J. B. Thaxter
Sperry Research Center, Sudbury, MA 01776

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SECTION 1
INTRODUCTION

This report covers the work performed on Contract No. N0014-82-C-0525 during the period July 1982 to August 1983. The basic goal of this program was to explain the physical basis of the improved Nb-Si-Si:H-Si-Nb tunnel junctions.

Substantial evidence has been accumulated during the course of this program which indicates that the localized states which are present in nonhydrogenated sputtered amorphous silicon barriers contribute to the larger current density observed at biases below the superconducting energy gap of the electrodes. The basic observations and the method of measuring the density of localized states at the Fermi level of the barrier materials are presented in the Appendix which is a reprint of a paper presented at the 1982 Superconductivity Conference [1]. More recent observations and theoretical speculations are included in this report.

SECTION 2

EFFECTS OF HYDROGEN CONCENTRATION ON DEVICE PROPERTIES

We have studied the effects of varying the hydrogen concentration in composite Si-Si:H-Si barriers. The results are summarized in Fig. 1. These data show that there is a relatively sharp threshold in hydrogen partial pressure for subgap leakage to be reduced by the addition of hydrogen to the 8 mT Ar pressure used for the sputtering plasma.

The existence of such a threshold is not surprising since it has been previously observed that the density of localized states at the Fermi level in sputtered hydrogenated amorphous silicon decreases exponentially with increasing hydrogen partial pressure. For example, Fig. 2 displays recent results obtained by Moustakas under qualitatively similar deposition conditions [2]. (It should be noted that Moustakas used substrate temperatures between 200-300°C in order to produce high quality photovoltaic material; we purposefully avoid such temperatures in order to produce high quality tunnel barriers.) Nevertheless the more complete study by the Exxon Research Laboratory group is relevant to our situation. We interpret the threshold for obtaining high-V_m devices as being caused by the rapid decrease in density of localized states. (V_m is the product of critical current multiplied by the subgap resistance measured at 2 mV.) Increasing the partial pressure of hydrogen beyond about 0.5 mT does not produce any further improvement in V_m either because further increases in the hydrogen concentration does not cause further lowering in the localized state density or because, perhaps more likely, the subgap leakage is limited by factors other than the density of localized states in the interior of the barrier.

The data of Fig. 1 represent the results of more than 25 runs. The data were not easily obtained because of unanticipated complications. Chief among these complications was a hydrogen "memory-effect" when the hydrogen partial pressure exceeded ~ 1 mT. Eventually we discovered that lower V_m resulted for the subsequent 4-6 runs if the H_2 partial pressure exceeded 1 mT, even though the hydrogen concentration in all these latter runs was

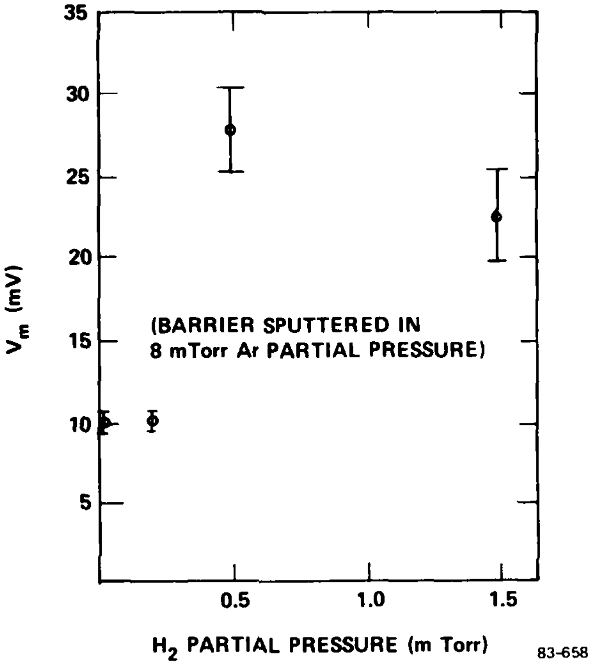

FIG. 1 Observed V_m as a function of partial pressure of H_2 in aSi/aSi:H/aSi composite barriers. The reduced V_m at the highest H_2 partial pressure may only be a confound (see text). Note the abrupt rise in V_m at lower partial pressure.

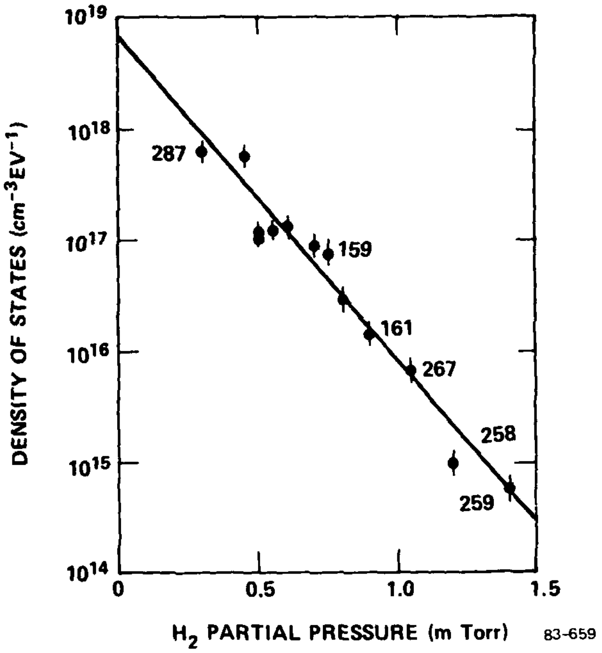

FIG. 2 Density of localized states at the Fermi level as a function of H_2 partial pressure for sputtered aSi/H layers (after Moustakas).

below 0.5 mT, and both the silicon and niobium targets were "thoroughly" cleaned by sputter etching. We suspect that hydrogen attached to the inner chamber or which had reacted with the silicon target acted to "poison" the lower niobium electrode's interface. We also had difficulty reproducing the desired current density following runs at H_2 partial pressure > 1 mT.

The lower V_m of the devices fabricated with the highest partial pressure of H_2 may only represent a confound due to factors relating to the "memory effect". However, the high V_m obtained with the highest H_2 partial pressure was obtained only at low current densities ($< 100\ A/cm^2$).

SECTION 3

DISTRIBUTION OF HYDROGENATED MATERIAL IN BARRIER

The original work made use of composite barriers whose nominal thicknesses of the Si, Si:H and Si layers were 8 A, 40 A, and 8 A respectively. The intended thickness ratios are 1:5:1. We have begun to suspect that initial rate of deposition of hydrogenated silicon is less than its equilibrium rate (after, say, 1 minute). We shall nevertheless use the intended thickness ratios in this discussion.

More recently we have varied the relative thicknesses of the aSi and aSi:H layers. Generally we find that the same device quality is obtained with significantly thinner aSi:H layers which are centrally positioned in the barrier. In fact the highest ratio of I(4 mV)/I(2 mV) = 40 obtained for a Nb-Si-Nb device was achieved with a composite Si-Si:H-Si barrier whose thickness ratios were 3:1:3. The current-voltage characteristics of this device at 4.3 K are displayed in Fig. 3. This device did not have the highest V_m observed probably because of the fact that the barrier was not sputtered cleaned before deposition of the counterelectrode. The pronounced "knee" at the superconducting energy gap is an indication of this (purposeful) omission in this particular experiment. We generally find that a pronounced "knee" is associated with a much smaller critical current. This observation strongly suggests that reducing localized states at the Fermi level in the center of the barrier is the most effective means of reducing subgap leakage. This naively suggests that either resonant or two-step tunneling is an important mechanism for opening up channels for subgap current beyond simple electrode-to-electrode tunneling. However, the complete observations described below do not obviously fit either a simple version of either resonant or two-step tunneling models.

We have also studied the effect on device properties of only slight reductions in the thickness of the central hydrogenated layer in composite barriers. For example "1:4:1" barriers rather than the original "1:5:1" barriers have produced devices with V_m = 29 mV as illustrated in Fig. 4.

Although these devices did not really have a much higher V_m than

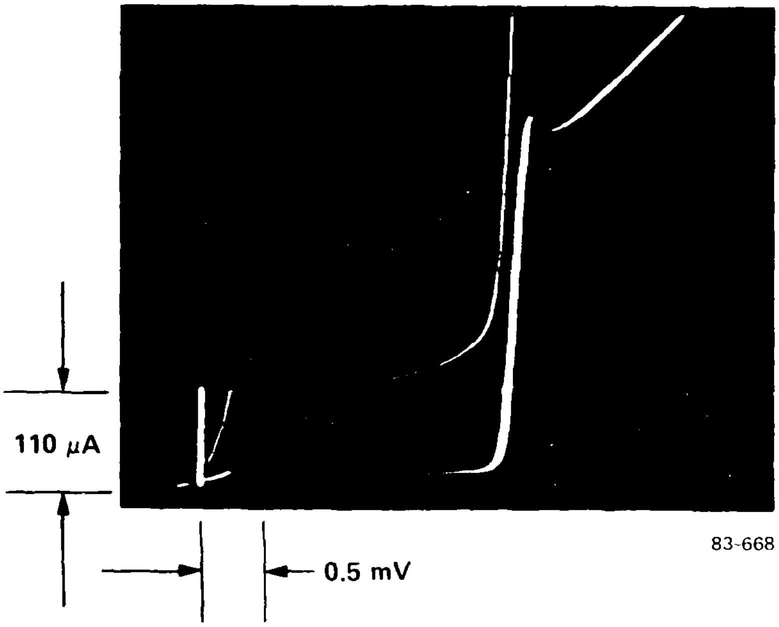

FIG. 3 Current-voltage characteristics of aSi/aSi:H/aSi devices with a nominal thickness ratio of 3:1:3. Ratio of I(4 mV)/I(2 mV) = 40. V_m is lower than otherwise expected because of "knee" at energy gap. Knee was probably caused by use of evaporated Nb counterelectrode; with our equipment this choice prohibited a sputter clean of the barrier before the counterelectrode deposition.

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FIG. 4 Current-voltage characteristics of Nb/aSi/aSi:H/aSi/Nb devices whose composite barrier had nominal thickness ratios of 1:4:1.

the "1:5:1" structure; they are more interesting from a manufacturing point of view. The "1:5:1" structures evidenced a decreasing V_m with increasing distance from the center of the target. For example, 7 cm away from the target center the V_m was observed to be as low as 10 mV. On the other hand, with a slightly thinner central aSi:H layer the V_m is essentially independent of radial position. (An increase in current density was still observed with increasing radial distance as it is with completely unhydrogenated barriers, but no variation in the ratio of I(4 mV)/I(2 mV) was observed.)

Part of the effect of radial distances on V_m is due to poor Nb counterelectrode material away from the deposition center as shown by comparing evaporated vs. sputtered counterelectrode experiments. This is probably due to pickup of H_2 and other contaminants at the edges of the discharge during the Nb counterelectrode sputter depostion.

We had planned to continue these studies by moving the position of the thin hydrogenated material across the barrier. We have not been able to complete these studies under the present circumstances. Perhaps, they would have been only of academic interest: the thin hydrogenated layer should "obviously" be centrally located. On the other hand, perhaps there could be a surprise, especially in light of the difficulties described below in uniquely fitting our observations to either a spin-flip scattering model or a resonant tunneling model. One slightly fanciful hypothesis that could accommodate an improved V_m independent of the position of the hydrogenated layer concerns the effect of the hydrogenated layer upon the subsequently deposited unhydrogenated layer. The upper unhydrogenated layer could have different structure which results in a lower state density at the upper electrode-barrier interface thereby reducing the importance of other conducting channels. This hypothesis is partially countered by the observation that the overall thickness for hydrogenated vs. nonhydrogenated barriers is very similar. Thus an a-Si layer on top of a-Si:H does not have a very different barrier height than plain a-Si.

SECTION 4
SPIN DENSITY

We used the only equipment currently available at Sperry to attempt to measure spin density. This was a Gunn oscillator placed in a magnetic field. On one end wall of the cavity we placed an amorphous silicon film. When the magnetic field is set for resonance and with a sufficient number of spins present in the cavity a frequency shift and change in bias current occurs for the Gunn diode.

The magnetic field was modulated at some convenient audio frequency. Even with phase sensitive detection, we could not measure any resonance signal from the aSi:H layers which were 1000-2000 A thick. We estimate the sensitivity of this apparatus to be capable of detecting about 5×10^{18} spins/cm^3.

The nonhydrogenated layers had a spin density of 10^{20}/cm^3, a value which is typical of many evaporated and sputtered silicon layers. The g-factor of the centers was 2.05, in agreement with the value which is commonly quoted for paramagnetic centers in aSi.

While these values are not surprising, they do confirm that our silicon barriers are not peculiar in any unsuspected way. The lower density of paramagnetic centers in the hydrogenated layers is of more direct interest, however. Most low values of spin density in hydrogenated silicon layers which are quoted in the literature are obtained from layers prepared when the ambient substrate temperature was 200°-300°C. (These higher temperatures are commonly used to prepare high quality photovoltaic material; our room temperature ambient substrates temperature is more suited to producing high quality tunnel barriers.) The spin density of less than 5×10^{18}/cm^3 directly shows that the conditions which we used (room temperature ambient, 8 mT partial pressure of Ar, 0.5 mT partial pressure of H_2 and a 10 cm target-to-substrate separation) are adequate to greatly reduce spin density.

We still anticipate further work on measurements of spin density in collaboration with Ed Cukauskas and Marty Nisenoff. They are looking into collaborating with another group at NRL which is interested in measuring spin density which results from imperfections in a wide class of semiconductor materials. This group has available more sensitive spectrometers than what we could assemble at Sperry. Any publishable results will, of course, be cleared with ONR and ONR support acknowledged.

SECTION 5
ZERO BIAS ANOMALY

Figure 5 displays the type of zero bias anomaly (ZBA) which we typically observe in our junctions which have niobium electrodes and silicon barriers. The anomaly is an increased differential conductance within a few mullivolts of zero bias. These data were obtained at 10-12 K in order to suppress the structure associated with the superconducting energy gap of the electrodes. The change in conductance (compared to the extrapolated value at zero bias) for a nonhydrogenated barrier is about 6-10 percent as shown in Fig. 5a, whereas the change in conductance for a composite aSi/aSi:H/aSi barrier or for a fully hydrogenated barrier is ~ 2 percent as shown in Fig. 5b and 5c.

According to standard theories [3,4], this type of ZBA is associated with spin flip scattering by an electron which is reflected from the paramagnetic center back into the electrode from which it emerged produced by localized states "near" the electrodes. (Stu Berman of IBM has told us that <u>all</u> previously observed such ZBA's have been associated with such spin flip scattering events in which the paramagnetic center responsible for the flip is within "one or two" lattice constants of the electrode.) It is therefore curious that there does not appear to be any difference between the magnitude of the ZBA associated with the fully hydrogenated layer (Fig. 5c) and that associated with composite barrier in which the hydrogenated layer is nominally ~ 8 A from the electrodes.

Thus we must assume that either the lower density of paramagnetic centers is not the reason for a smaller ZBA or else assume that the theory is incomplete. We examine below evidence that the reduction in localized states in the <u>center</u> of the barrier seem to be the most important reason for the improvement in subgap leakage current brought about by hydrogenation. An area in which the existing theory might be expanded is the two-sided nature of real devices which in some manner could increase the importance of states near the center of the barrier in spin-flip scattering. Specifically one wonders if a "resonant" spin-flip scattering channel exists, with the position of the

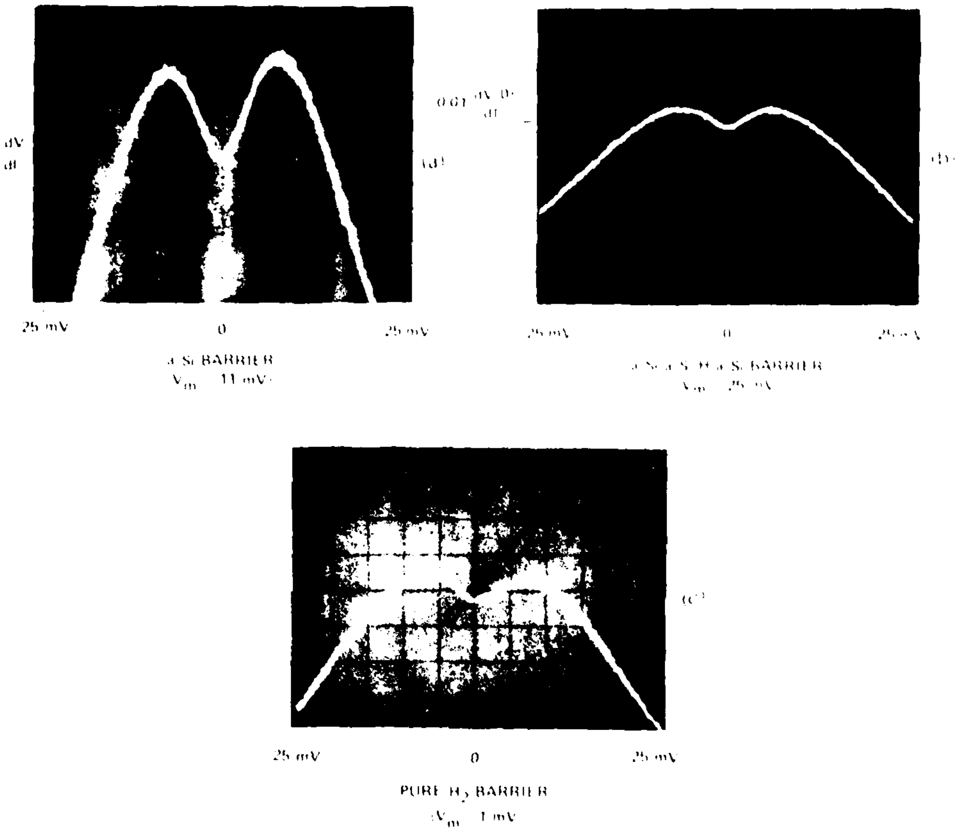

FIG. 5 dV/dI vs. V for three different Nb/Si/Nb structures at 10-12 K.
(a) aSi barrier
(b) aSi/aSi:H/aSi composite barrier with nominal thickness ratio 1:5:1.
(c) aSi:H barrier

resonant energy level near the barrier center, compensating for the weaker spin-flip probability.

Further experiments are called for and some are planned. These are experiments in which the ZBA is studied as a function of applied magnetic field. ZBA's which are caused by spin-flip scattering have a unique signature for fields > 3 T at ~ 2 K. E.J. Cukauskas at NRL is setting up a superconducting magnet which can attain fields of ~ 7 T. Devices fabricated on the current contract will be supplied to him; any results which are publishable will be cleared through ONR and the support of ONR will be acknowledged.

SECTION 6
LOW FREQUENCY NOISE IN JOSEPHSON DEVICES AND SQUIDS

There is another aspect of the work on this contract which is incomplete and the subject of a collaborative effort. We suggested in the proposal for this contract that the additional conduction channel which is provided by the localized states in the barrier could be an additional noise source. We suspected this current noise would manifest itself at low frequencies since thermally activated processes should operate slowly at cryogenic temperatures. Indeed, we were inspired to think of this possibility because the Sperry Computer Systems division had observed large 1/f noise in SQUID magnetometers fabricated for the Navy. These devices were made using older Sperry processing techniques which resulted in larger subgap leakage currents than observed in any device studied under this contract.

In the interim Bob Buhrman of Cornell had obtained evidence that "traps" within a niobium oxide barrier could raise the level of 1/f noise in junctions or SQUIDs. We decided to collaborate with Buhrman. His "traps" are conceptually the same as our "localized states".

We have furnished Buhrman with "pogo pin" (spring loaded) contacts and a map of some of our chips. After his students fabricate a holder which can accommodate our chips, we will supply him a variety of chips (aSi, aSi:H as well as composite barrier devices) to measure 1/f noise as a function of temperature. Any publishable results will, of course, be cleared through ONR and ONR support acknowledged.

SECTION 7

DIFFUSION OF HYDROGEN IN aSi

A number of observers have questioned whether the use of hydrogen to improve the I-V characteristics of the composite barriers is truly a suitable method of improving device characteristics because the hydrogen could easily diffuse to the electrodes. There are several reasons to believe that this method is satisfactory. The most compelling reason is experimental. Figure 6 displays the variation in V_m as a function of time of annealing at 150-200°C for composite barrier devices. This temperature is at least 30°C higher than any usually performed processing steps. Note that the V_m usually improves for short annealing times.

A second comforting aspect is that bi-layer composite barriers (aSi/aSi:H) appear to yield similar characteristics as trilayer (aSi/aSi:H/aSi) composite barriers. This suggests, perhaps, that the implantation of H^+ into the lower electrode during sputtering in a partial hydrogen plasma is the mechanism responsible for the reduction in V_m of a uniform aSi:H barrier.

Finally, there is no compelling theoretical reason to believe that the hydrogen can diffuse to the electrodes in any significant time or temperature of interest. No measurement of the diffusion of hydrogen in sputtered-deposited aSi:H has been reported. However, two measurements of the diffusion of deuterium in deuterated aSi which has been deposited by glow discharge have been reported. Carlson, et al. [5] determined that the diffusion coefficient D of deuterium in aSi:D was

$$D = 1.7 \times 10^{-2} \exp -q/kT\ (1.53 \pm 0.15)V \quad cm^2$$

This was measured at T > 500°C. More recently, Matsumura et al. [6] have measured the diffusion coefficient in glow discharged-deposited aSi:D and determined that the diffusion coefficient is about an order of magnitude lower than the measurements of Carlson, et al.

Let us consider several variations of the worst-case possibilities. At 300°K (near room temperature) the mean value of the diffusion coefficient

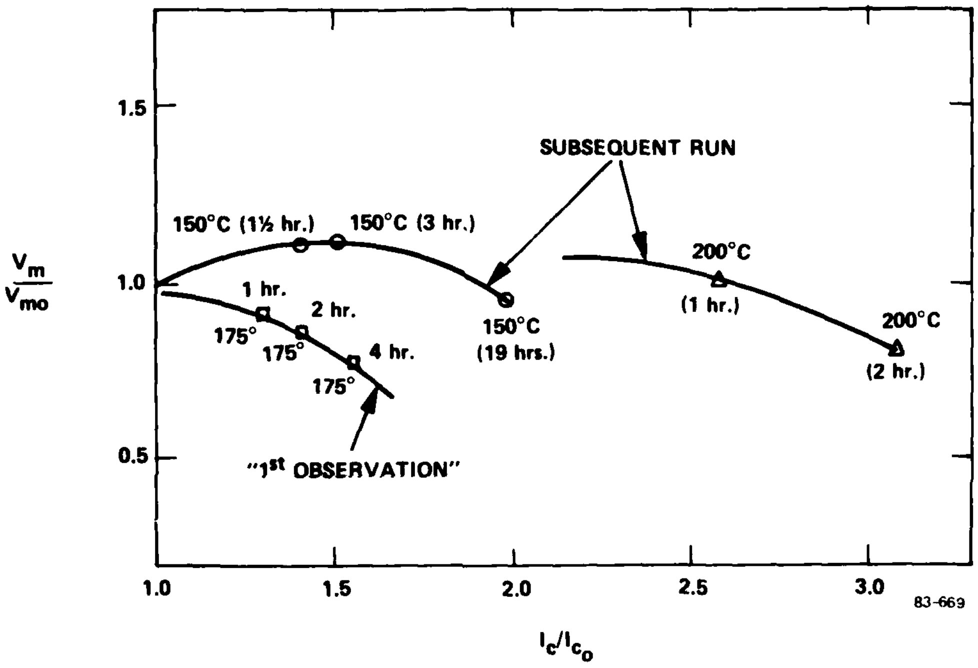

FIG. 6 Annealing data on several Nb/aSi/aSi:H/aSi/Nb device runs.

according to Carlson is $D = 3.55 \times 10^{-28}$ cm^2 s^{-1}. In order to move 8 A (the central value of the separation of the niobium electrode from the hydrogenated layer) the time required would be $t \sim x^2/D \sim 0.5$ M year. At 423 K, the highest temperature used in our common processing, the diffusion coefficient even assuming the activation energy is only 1.38 eV (= 1.53 - 0.15 eV) is 6.4×10^{-19} cm^2 s^{-1}. To diffuse 8 A, a time of 2 1/2 hours would be required. It is important to note that in each case a worse case has been assumed: prolonged storage at room temperature with a high diffusion coefficient or the highest diffusion coefficient consistent with any measurements at elevated temperatures. We therefore cannot definitely conclude that the annealing data of Fig. 6 can be explained by diffusion of hydrogen to the electrodes.

We have also prepared similar structures using deuterium rather than hydrogen. The deuterated barriers have I-V characteristics and annealing behavior at 185°C essentially the same as hydrogenated barriers.

SECTION 8

THEORETICAL CONSIDERATIONS

The introduction of localized states into an ideal tunnel barrier can have several effects as illustrated in Fig. 7. The average tunneling barrier height $<\phi>$ will be lowered and it is this average quantity which enters into the standard formula for tunnel currents [7]. While it is true that the hydrogenated barrier probably does have a slightly lower current density than unhydrogenated barriers of the same thickness, we do not believe that this constitutes direct evidence of this insight. First, the hydrogenated material has a wide energy gap and this could translate into a higher tunneling barrier independent of the presence of localized states. Second, the major effect of the localized states could be to permit resonant tunneling. Resonant tunneling could by itself increase tunnel conductance. However, resonant tunneling should increase the tunnel conductance of all transitions including those which are allowed even if there were no localized states. However, the major effect of adding hydrogen is to reduce subgap currents -- especially above half the gap voltages. Adding a resonant tunneling channel should not obviously effect I(4 mV)/I(2 mV) but hydrogenation does, in fact, increase this ratio. It is therefore difficult to ascribe to resonant tunneling the improvements brought about by hydrogenation.

There are other channels of conductance which localized states make possible, including two-step, nonresonant tunneling as illustrated in Fig. 8. The thermally activated tunneling transitions originating (or terminating) in hybridized states are consistent with the observations. ("Hybridized" states were introduced by Halbritter; according to him they are mixtures of the extended states of the electrodes and the localized states of the barrier. The hybridized states which can most significantly affect tunneling are located "near" to the electrodes, according to Halbritter.) We view that the suggestion that hybridized states could explain the observations as being certainly very preliminary and useful at present only as a hypothesis to guide further experiments.

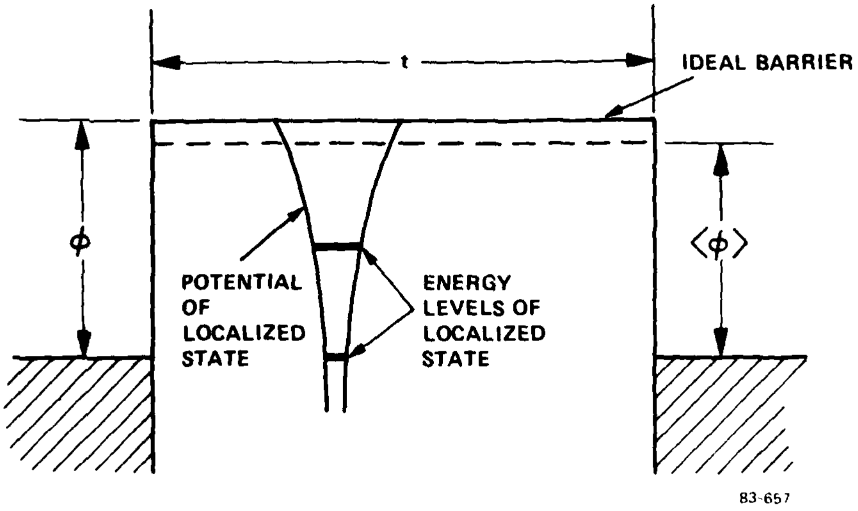

FIG. 7 Energy vs. distance diagram of an "ideal" one dimensional barrier and the effect of the addition of a localized state.

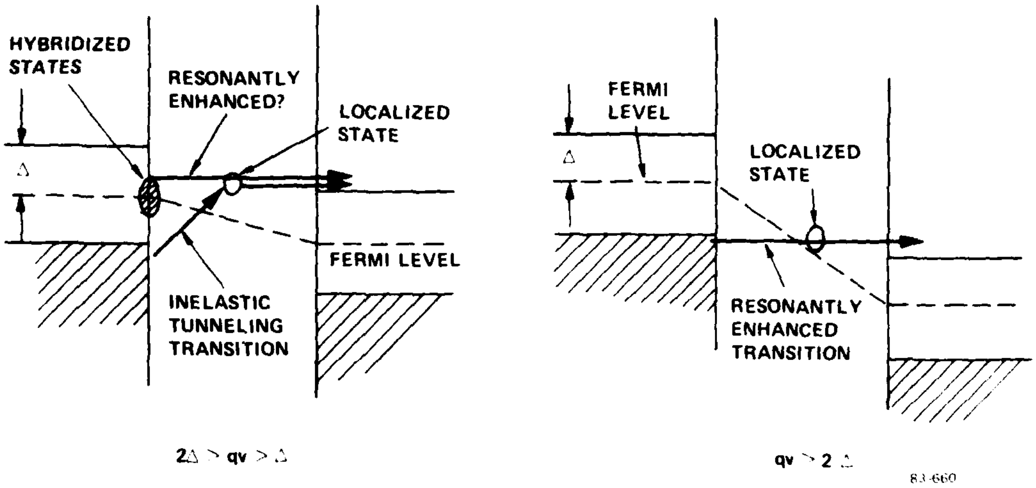

FIG. 8 Possible tunneling transitions in a "nonideal" barrier
(a) Voltage bias less than energy gap of electrodes
(b) Voltage bias greater than energy gap of electrodes.

SECTION 9
CONCLUSIONS

We have presented a great deal of circumstantial evidence that localized states within the barrier of a tunnel junction can produce imperfect tunneling characteristics. A complete understanding of this situation is lacking. The theoretical situation is muddled, although we have no doubt that localized states are ultimately responsible for the imperfect I-V characteristics. We expect secondary characteristics (1/f noise) of tunnel junctions will eventually be correlated with the presence of localized states within the barrier.

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APPENDIX

Improved Nb-Si-Nb SNAP Devices

IMPROVED Nb-Si-Nb SNAP DEVICES*

H. Kroger, L.N. Smith, D.W. Jillie and J.B. Thaxter
Sperry Research Center
100 North Road
Sudbury, MA 01776

Abstract

We have compared the tunneling characteristics of Nb-Si-Nb junctions whose amorphous silicon barriers have been sputtered in pure Ar with those sputtered $Ar-H_2$ plasmas as well as in various combinations. We observe lower subgap currents with composite barriers which comprise a central region which is hydrogenated but which is sandwiched between two thin unhydrogenated layers. The improved tunneling characteristics may be associated with the lower density of localized states in the hydrogenated silicon.

Introduction

In recent years there have been many studies of amorphous silicon as a major constituent of tunnel barriers in Josephson devices. Evaporated silicon was used by Moore *et al.* on V_3Si[1] and on Nb_3Sn[2] base electrodes and by Kwo *et al.* on Nb_3Al base electrodes.[3] Rudman and Beasley have studied the properties of oxidized a-Si barriers on a variety of materials.[4] Amorphous silicon barriers produced by rf glow-discharge deposited Si have been studied by Shinoki *et al.*,[5] and Shoji *et al.*[6,7] with NbN electrodes. Sputtered amorphous Si (a-Si) and sputtered hydrogenated amorphous silicon (a-Si:H) have been described by Kroger *et al.*[8-10] and by Smith *et al.*[11] with Nb electrodes, by Jillie *et al.* in NbN/Nb devices,[12] and by Cukauskas with NbN electrodes.[13]

This paper will describe the initial phase of a systematic study of the effect of the composition of sputtered silicon barriers on the properties of Josephson devices. All device structures discussed are fabricated by the selective niobium anodization process (SNAP).[9] The inherent reproducibility of SNAP permits meaningful comparison between devices fabricated at different times which have variations in barrier composition.

Fabrications, Especially Barrier Oxidations

One important feature of SNAP is that the base electrode, barrier and counterelectrode are deposited before any lithographic process is initiated. However, even before the counterelectrode is deposited two processing steps and two process monitoring steps are usually performed. The processing steps are (1) an exposure of the barrier to oxygen[4] and (2) a sputter-clean of the barrier at such low power that it is presumed that only loosely bound oxygen or other adsorbed materials are removed.[illegible]

The optical reflectivity of the Si layer on the Nb substrate can be conveniently measured[illegible] both before and after the oxidation step is performed. Fig. 1 presents data on the reflectivity of a-Si and a-Si:H layers on niobium. Each datum point represents a separate measurement following a given time interval of deposition. For these layers (and for all other layers described in this paper) the sputtering conditions were: 8 mT pressure of Ar for the a-Si depositions; 8 mT partial pressure of Ar and 0.5 mT partial pressure of H_2 for the a-Si:H depositions; and 0.3 W/cm² of applied rf power for both materials. Deposition rates of ~ 30 and [illegible] Å/min. were obtained for the a-Si and a-Si:H, respectively.

Other workers have found that devices made both with evaporated Si layers which were thermally oxidized[4] and with glow discharge deposited silicon layers which were plasma oxidized[7] had properties which were so sensitively dependent upon oxidation conditions that it is clear that a substantial fraction of the tunneling barrier was converted to a silicon oxide. This has *not* been our experience with thermally oxidized, sputtered silicon barriers. The normal resistance and critical current density of devices made with sputtered silicon is neither a sensitive function of oxidation temperature (between 80-150 C) nor of the time interval to which the barrier is exposed to dry oxygen. Furthermore, the observed reflectivity change when the sputtered Si is exposed to O_2 is consistent with the conversion of only about 3 Å of Si to an oxide. This occurs within the first ten seconds of admitting oxygen to the sputtering system and no further change in reflectivity is observed.

The practical effects of our barrier oxidation are to lower conductivity and reduce subgap leakage current. (There have been several experiments in which low subgap leakage has been observed without performing the oxidation step but these observations are beyond our usual processing experiences.)

From the above discussion we suppose the function which our oxidation step performs is either to patch pinholes in the barrier, or, more likely, to passivate the surface, or to cause a change in Schottky barrier height at the silicon-upper electrode interface. The conversion of a significant portion of the barrier to an oxide seems improbable.

Following the oxidation and sputter cleaning of the barrier, the SNAP fabrication continues with the deposition of the counterelectrode and this is in turn followed by the first photoresist patterning. Isolated Josephson junctions are formed by anodizing through the upper niobium layer, while the devices themselves are protected from anodization by a photoresist (or other insulator) mask.[9]

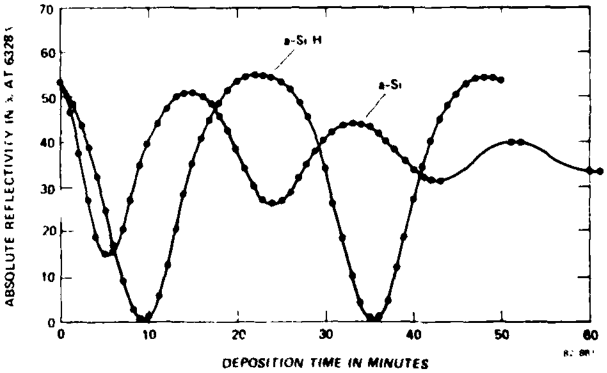

Fig. 1. Reflectivity of a-Si and a-Si:H layers on Nb as a function of deposition time.

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a-Si and a-Si:H Barriers

The I-V characteristics of a Nb - a-Si - Nb device are presented in Fig. 2a. Technologically attractive features of such devices are their low specific capacitance (~ 2.5 μF/cm^2 for a current density of several hundred A/cm^2)[11] and their uniformity and reproducibility.[10,11,15] Although these devices have been successfully operated in small scale integrated circuits,[16] it would be desirable for many applications to have lower leakage currents for applied voltages which are less than the sum of the energy gaps of the electrodes, V_g. For example, the V_m parameter (= I_cR_s), where I_c is the critical *Josephson current* and R_s is the subgap resistance, is only 8-12 mV for such structures (when R_s is measured at 1.5 - 1.7 mV).

These a-Si barrier devices consistently show excellent threshold curves (variation of I_c as a function of applied magnetic field), indicating uniform Josephson current density. This observation together with the above noted uniformity and reproducibility suggests that gross imperfections (metallic shorts, for example) are not responsible for the excess subgap current. The possibility of improving the barrier on an atomic scale by the use of a-Si:H was therefore investigated.

Fig. 2b displays the I-V characteristics of a Nb - a-Si:H - Nb device which had the same nominal thickness (~ 56 Å) as the a-Si device of Fig. 2a. The normal resistance R_N of the device is about what one would expect for an a-Si barrier of the same thickness. (We did not measure the optical thickness of this a-Si:H barrier.) We attribute the greatly increased subgap current of the a-Si:H device to contamination of the surface of the Nb electrode(s) by hydrogen which can lower the transition temperature of Nb. This interpretation is confirmed by comparing these results to the I-V characteristics displayed in Fig. 2c which are obtained from the structure shown in cross section in Fig. 2d. This structure has a composite trilayer barrier with thin (nominally 8-9 Å) a-Si layers sandwiching an a-Si:H layer of nominal thickness of ~ 39 Å. R_N of this structure was also about what one would expect for an a-Si barrier of the same total thickness.

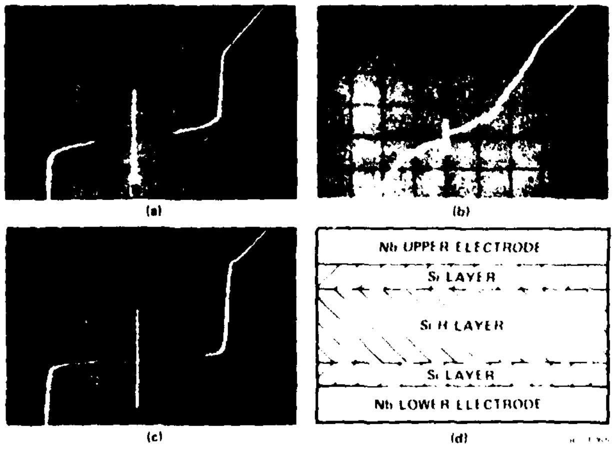

Fig. 2. I-V characteristics of Nb devices at 4.2 K whose barriers are a-Si, a-Si:H and a composite of a-Si, a-Si:H and a-Si are shown in (a), (b) and (c) respectively. The structure of the composite barrier is shown in (d).

The composite barrier device has V_m = 28 mV, measured at 2 mV. The I_cR_N product of the a-Si barrier is only 1.3 mV, while the I_cR_N of the composite barrier is 1.6 mV, a significantly higher value. The contrast between the I-V characteristics of the a-Si:H device and the composite barrier device suggests that several monolayers of sputtered a-Si are sufficient to essentially completely cover the lower Nb electrode. Similar composite barriers when substituted for simple a-Si barriers in NbN-Si-Nb devices have also resulted in lower subgap currents.[17]

Physical Properties of a-Si and a-Si:H

Table I presents a summary of physical properties of a-Si and a-Si:H which are relevant to the behavior and the fabrication of tunnel junctions whose barriers are formed of these materials. We emphasize that material properties cannot be categorized in general with the simple nomenclature "a-Si" or "a-Si:H". The properties of these materials span a continuous spectrum and are controlled by the method of deposition, substrate temperature, subsequent thermal annealings, hydrogen content, etc. An extensive review of the properties of sputtered a-Si:H has recently been published by Paul and Anderson.[18]

Most amorphous silicon materials have a high density of states within the semiconductor band gap compared to crystalline semiconductors. States near the center of the gap are localized but their density may be so large that "variable range hopping" (thermally activated tunneling) between these states can dominate the conduction, especially below room temperature.[19] Hydrogenation of amorphous silicon can greatly reduce the density of states within the energy gap by satisfying the "dangling bonds" which are present in tetrahedrally bonded amorphous semiconductors.[20] The density of paramagnetic centers[21] (which are presumably the sites for variable range hopping) also is reduced by hydrogenation.

The electronic states of these materials which are near the Fermi level can be expected to contribute to their behavior as Josephson tunnel barriers. The density of localized states at the Fermi level can be conveniently estimated by measuring the conductivity as a function of temperature. According to Mott's variable range hopping theory,[22] the conductivity

TABLE I
Physical Properties of a-Si and a-Si:H

	a-Si	a-Si:H
Resistivity (Ω cm)	10^3 – 10^5*	10^7 – 10^{12}*
ϵ/ϵ_0 (~ 1 MHz)	~ 13*	~ 8*
Index (at 6328 Å)	4.4*	3.0*
Spin Density (cm^{-3})**	$\gtrsim 10^{19}$	~ 0
$N_t(F)$ (cm^{-3}-eV^{-1})	$\lesssim 10^{20}$ 2 × 10^{18}*	$\gtrsim 10^{15}$ $\lesssim 10^{16}$

*For materials used in this paper
**Not measured for our materials

is given by

$$\sigma(T) = \sigma_o(T) \exp -\left(T_o/T\right)^{\frac{1}{4}} \qquad (1)$$

where

$$T_o = \frac{128}{9\pi} \; \frac{1}{r_o^3 \, N_E(F) \, k} \qquad (2)$$

and where $N_E(F)$ is the volume density of localized states per unit energy, k is Boltzmann's constant and r_o is the decay length of the localized state whose wave function is ψ, i.e.,

$$\psi = \psi_o \exp -\left(r/r_o\right) . \qquad (3)$$

Several authors[23,24] have found an alternate expression derived by Kirkpatrick,[25] which is based on percolation theory, to yield a more reliable determination of both $N_E(F)$ and r_o. Kirkpatrick's formula is

$$\sigma = 0.022 \left(C/r_o\right) \left(T_o/T\right)^{0.35} \exp -\left(T_o/T\right)^{\frac{1}{4}} \qquad (4)$$

where C is a constant, generally supposed to depend upon material parameters which are approximately the same for crystalline materials (for which they have been measured) as for amorphous materials.

Fig. 3a displays plots of log σ vs. $T^{-\frac{1}{4}}$ and log $\sigma T^{0.35}$ vs. $T^{-\frac{1}{4}}$ for 0.2 µm thick a-Si layers prepared in the same manner as our a-Si tunnel barriers. The straight line plots are usually interpreted as evidence of variable range hopping. From these plots and using (4) we find $r_o \approx 10.6$ Å and $N_E(F) \approx 2.2 \times 10^{18}$/cm^3 - eV.

Thick layers (~ 0.2 µm) of the a-Si:H material do *not* obey a σ vs. $T^{-\frac{1}{4}}$ rule. Instead, the conductivity of the a-Si:H layer obeys a thermally activated conduction law, i.e.

$$\sigma(T) \sim \sigma_o \exp -\left(\frac{qV_a}{kT}\right)$$

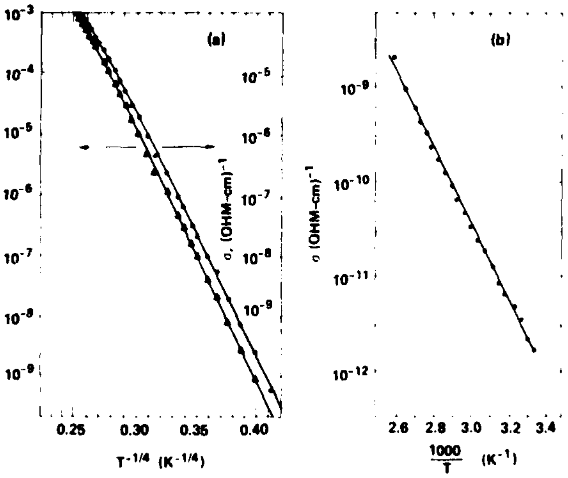

Fig. 3. (a) log σ and log $\sigma T^{0.35}$ vs. $T^{-\frac{1}{4}}$ for a 0.2 µm thick a-Si layer. (b) log σ vs. 1000/T for a 0.2 µm thick a-Si:H layer.

where the activation energy $V_a \approx 0.6$ V as illustrated in Fig. 3b. Unlike the a-Si layers, the a-Si:H layers are photoconductive. These observations indicate that the hydrogenation has removed enough localized states from within the gap of the a-Si:H so that variable range hopping at the Fermi level is not the dominant conduction mechanism near room temperature.

The density of localized states generally increases rapidly towards the band edges.[19,20] Because of real contact potentials and band bending, the value deduced above for the density of localized states in the *bulk* of the a-Si should be only considered a lower limit on the density of localized states at E_F in a thin tunneling barrier device.

Effect of Localized States on Tunneling Characteristics

There have been both experimental and theoretical indications that localized states in the barrier can affect subgap current in superconducting junctions. Shen and Rowell observed a correlation between the magnitude of a "zero bias anomaly" (ZBA) and subgap leakage in Sn-I-Sn tunnel junctions.[26] The ZBA which they observed is an increase in the differential conductance dI/dV as a function of applied bias V within a few millivolts of V = 0. Shen and Rowell established a relation between the ZBA and the presence of accidentally introduced magnetic impurities[26] by applying magnetic fields large enough to qualitatively change the shape of the ZBA according to Appelbaum's theory.[27]

We have also observed a ZBA in our junctions at 10-16 K. (Below the T_c of the electrodes the superconducting structure prohibits observation of the ZBA unless a strong enough magnetic field is applied to quench the superconducting state.) Like Shen and Rowell we observe a correlation between the magnitude of the ZBA and excess subgap current. The composite barriers with $V_m > 20$ mV have a 1-2% ZBA; the a-Si with $V_m \approx$ 8-12 mV have a 4-6% ZBA. We also observe, as did these authors, a correlation between a larger ZBA and greater curvature in dI/dV. However, we emphasize that we have not yet proven the relevance of the ZBA which we have observed to the presence of known localized states which should have a g-factor of [illegible] in a-Si.[31] Experiments in high magnetic fields might establish such a connection.

A number of authors have recently discussed several ways in which localized states within a barrier can affect tunnel conductance.[28] Among these are resonant tunneling, incoherent tunneling and hybridization of the extended states of the electrodes with the localized barrier states. Halbritter has discussed the hybridization of the states in niobium oxide barriers with the conducting states in niobium electrodes[29] and suggested that hybridized surface states can be formed at energies within the bulk superconducting energy gap. Such states could obviously contribute to "subgap" currents. While this theory must be modified for the paramagnetic states of a-Si barriers, the physical picture of how the extended states of the electrodes mix with localized states is intriguing. One might expect such an interaction to function as a pair weakening mechanism for the paramagnetic states in a-Si.

Establishing firm contact with either the previous experiments[26] or theory[29] will require further refinements of theory and more detailed understanding of the composite barriers. Both Halbritter's theory[29] and that of Anderson[30] on scattering by magnetic impurities in barriers requires the localized states to be "close" to an electrode. We do not yet know the extent to which the central hydrogenated layer contributes to a lower density of localized states within, say, 2-6 Å of the electrodes or even theoretically how close to the electrodes the localized state density must be reduced to improve device properties.

Conclusions

The quality of Nb-Si-Nb Josephson devices with sputtered a-Si barriers can be substantially affected by sputtering Si barriers in a partial pressure of H_2. Lower subgap currents (higher V_m) have been observed in composite barriers in which the majority of the barrier is formed of a-Si:H. We suggest that the lower density of localized states in the a-Si:H material may be the mechanism responsible for our improved tunnel junctions. Further contact with the physics of localized states within semiconductors may yield further improvements in properties of devices which incorporate such materials as tunnel barriers.

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