

## Resistance Fluctuations Due to Hydrogen Diffusion in Niobium Thin Films

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Fluctuations of the number of protons ( $H^+$ ) that scatter conduction electrons dominate low-frequency resistance fluctuations in Nb films. The excess-noise spectra  $S_V(f, T)$  obey a scaling law:  $fS_V(f, T)/(\delta V^2(T)) = g(f/D(T))$ ; for our geometry at  $260 < T < 370$  K,  $S_V(f, T) \propto c_0(T)/f^\alpha$ ,  $\alpha = 0$  for  $f \ll D/(\pi L^2)$  and  $\alpha = \frac{3}{2}$  for  $f \gg D/(\pi L^2)$ ,  $c_0$  is the  $H^+$  concentration,  $L$  is the film length, and the  $H^+$  diffusion coefficient is  $D(T) = D_0 e^{-E/kT}$  with  $D(300 \text{ K}) \approx 10^{-6} \text{ cm}^2/\text{s}$  and  $E \approx 0.23 \text{ eV}$ . Studies of  $1/f$  noise evoke comparable mechanisms.

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Fluctuation spectra reflect the dynamics of the underlying physical processes and may thereby reveal phenomena that are obscured in conventional experiments. Small conductors commonly display low-frequency resistance fluctuations  $\delta r(t)$ , often with power spectral densities  $S_r(f) \propto f^{-\alpha}$  ( $\alpha \approx 1$ ). The physical origins of this ubiquitous “ $1/f$  noise” have escaped discovery despite extensive research.<sup>1</sup>

Some features of resistance fluctuations have emerged. Superposition of thermally activated processes<sup>2</sup> can represent the spectra and temperature dependence observed in metal films.<sup>3</sup> Fluctuations in the scattering rather than the trapping of conduction electrons have been proposed.<sup>1,4,5</sup> Tensor fluctuation correlations observed in Bi films<sup>6</sup> suggest anisotropic scatterers.<sup>6,7</sup> Temperature fluctuations have been excluded<sup>8</sup> except at a cryogenic phase transition<sup>9</sup> and noise generated by surface reactions and the approach to melting has been observed.<sup>10,11</sup> Defect and impurity scattering fluctuations have been recognized as potential sources of  $1/f$  noise, but their role is yet to be demonstrated.

Here we report studies of the resistance fluctuations in Nb films that identify and characterize the mechanism of the dominant low-frequency noise. Its level can be predictably reduced from the usual level of other metal films<sup>12,13</sup> by two orders of magnitude. Having observed that the primary noise in niobium films was associated with hydrogen impurities,<sup>14</sup> we have now analyzed the thermally activated dynamics of this noise process and identified the physical mechanism unequivocally. Fluctuations in the resistance of a film segment occur as protons randomly transit only the ends of the segment (since the film surface is impermeable to  $H^+$ ) thereby changing the total number  $N$  contained in the segment.  $N$  is too large to allow resolution of discrete events.<sup>15</sup> The general features of resistance fluctuations generated by scatterer migration are worked out.

Five-probe resistors (Fig. 1) were subtractively patterned from 120-, 190-, and 240-nm-thick Nb films sputtered onto highly polished  $0.010 \times 0.5 \times 0.5$ -in.<sup>3</sup>

sapphire substrates; photoresist patterns were transferred to Nb films by use of either a standard chemical etch (1:4:5 solution of HF:HNO<sub>3</sub>:H<sub>2</sub>O) or nonreactive sputter etching in an Ar<sup>+</sup>-ion mill. Four or five specimens having widths  $w$  and half-lengths  $L$  in the ranges  $0.7 \mu\text{m} \leq w \leq 32 \mu\text{m}$  and  $20 \mu\text{m} \leq L \leq 1050 \mu\text{m}$  were formed on each of fourteen substrates. Room-temperature resistivities  $\bar{\rho}(300 \text{ K})$  ranged from 17 to  $30 \mu\Omega \text{ cm}$  with residual resistivity ratios  $\text{RRR} = \bar{\rho}(300 \text{ K})/\bar{\rho}(10 \text{ K})$  ranging from 2.0 to 4.5. Various methods were used to make contacts.<sup>14</sup> Subtractive patterning is believed to have introduced hydrogen into all specimens; mean hydrogen concentrations  $c_0$  determined from noise magnitudes (see below) were typically 0.03 and 0.3 at.% for sputter and chemical etching, respectively. Further acid or ion-mill exposure resulted in  $c_0$  as high as 7 at.%. Hydrogen does not penetrate the niobium surface except when its oxide coating is absent during sputtering or etching.

Noise was measured with the specimen in the ac Wheatstone bridge (Fig. 1). Fluctuations in the resistances  $r_1$  and  $r_2$  of each specimen half produced a bridge imbalance that was detected with a PAR124A lock-in amplifier. The lock-in output  $\delta V(t) \approx G_0 I_0 [\delta r_2(t) - \delta r_1(t)]$ , where  $G_0 = 7.07/s$ ,  $s$  is the lock-in sensitivity (in  $V_{\text{rms}}$ ), and  $I_0$  is the amplitude of the bridge current. The lock-in output was filtered and fed directly into an HP5420A spectrum analyzer or

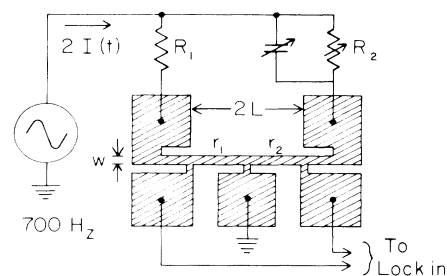


FIG. 1. Circuit diagram for ac noise measurement with five-probe specimen.

recorded on a Racal STORE-4DS FM data recorder for later analysis. Excess-noise spectra  $S_V(f)$  (measured for  $300 \mu\text{Hz} \leq f \leq 300 \text{ Hz}$  with a 700-Hz carrier) were proportional to  $I_0^2$  and free of contact noise. Negligible noise above background was observed with wire-wound resistors replacing the specimen.

Consider an infinitely long Nb conductor of cross section  $A$  containing dissolved hydrogen described by a local concentration  $c(\mathbf{x}, t) \ll 1$ . Fluctuations  $\delta N(t) = n_a \int_{\Omega_0} \delta c(\mathbf{x}, t) dx$  in the number  $N$  of hydrogen ions in a segment of length  $L$  result from fluctuations  $\delta c(\mathbf{x}, t)$ , where  $\Omega_0 = LA$  and  $n_a$  is the atomic density. The mean resistivity  $\bar{\rho}$  of bulk Nb increases with  $c_0$  by an amount  $\rho_0 = \beta c_0$ ,  $\beta \approx 0.65 \mu\Omega \text{ cm/at.}\%$ .<sup>16</sup> Thus, number fluctuations cause fluctuations in the segment resistance  $\delta r(t) = \gamma \delta N(t)$ , where  $\gamma \approx \beta/n_a A^2$ . (Internal variation of  $\beta$  with proton location is neglected.) Fluctuations  $\delta c(\mathbf{x}, t)$  evolve according to the diffusion equation  $(D\nabla^2 - \partial/\partial t)\delta c(\mathbf{x}, t) = 0$ . The power spectral density of  $\delta r(t)$  has been calculated.<sup>17</sup> The problem is reduced to one dimension by the surface oxide and substrate which prevent proton entrance and departure through surfaces other than the segment ends.

We have calculated the spectrum of the difference of fluctuations in the resistances  $r_1$  and  $r_2$  of two adjacent segments (appropriate to our bridge measurements) and find  $fS_V(f)/\langle \delta V^2 \rangle = 2P(\theta) - P(2\theta)$ , where  $\theta(f) = (f/f_c)^{1/2}$ ,  $f_c = D/\pi L^2$ ,  $P(\theta) = \theta^{-1}[1 - e^{-\theta}(\sin\theta + \cos\theta)]/\pi$ , and  $\langle \delta V^2 \rangle$  is the variance. At high frequencies  $f_c S_V(f)/\langle \delta V^2 \rangle \approx 3/(2\pi)(f/f_c)^{-3/2}$  while at low frequencies  $f_c S_V(f)/\langle \delta V^2 \rangle \approx 4/3\pi$ .<sup>18</sup> Extrinsic parameters are suppressed by considering resistivity fluctuations  $S_\rho(f) = (GI_0 \bar{r}/\bar{\rho})^{-2} S_V(f)$  which (assuming  $\langle \delta N^2 \rangle = \langle N \rangle$ ) have a variance  $\langle \delta \rho^2 \rangle \approx c_0 \beta^2 / N_a = \rho_0^2 / N_0$ , where  $N_a = 2n_a \Omega_0$ ,  $N_0 = c_0 N_a$ , and  $r = r_1 + r_2$  ( $r_1 \approx r_2$ ).

Temperature dependence enters  $S_\rho(f, T)$  through  $D(T)$  and  $c_0(T)$  [i.e.,  $f_c(T)$  and  $\langle \delta \rho^2(T) \rangle$ ]. The normalized spectrum  $fS_\rho(f, T)/\langle \delta \rho^2(T) \rangle = g(f/f_c(T))$  may be written as a function  $g$  of the single variable  $f/f_c(T)$ . A plot of  $fS_\rho(f, T)/\langle \delta \rho^2(T) \rangle$  vs  $\log[f/f_c(T)]$  is expected to yield a universal curve independent of temperature. While the form of  $g$  depends on the geometry, this scaling with  $f/f_c(T)$  generally holds for diffusion noise spectra since  $D$  and  $t$  enter the diffusion equation only as the product  $Dt$ .

The room-temperature excess noise of specimen ND-1, shown in Fig. 2, closely resembles the model diffusion noise spectrum. Curve  $a$  is the usual log-log plot of  $N_a S_\rho(f)/\bar{\rho}^2$  versus frequency, while curve  $b$  is a linear plot of the normalized spectrum  $fS_\rho(f)/\langle \delta \rho^2 \rangle$  vs  $\log[f/(1 \text{ Hz})]$ . The variance  $N_a \langle \delta \rho^2 \rangle \approx 1.6 \pm 0.3 (\mu\Omega \text{ cm})^2$ , obtained by numerical integration of  $S_\rho(f)$ , implies a hydrogen concentration  $c_0 \approx 0.04 \text{ at.}\%$  (typically uncertain by a factor of 2). The solid

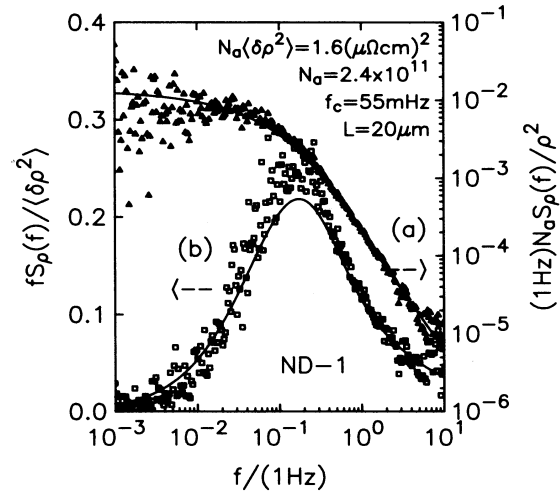


FIG. 2. Plots of, curve  $a$ ,  $\log[(1 \text{ Hz})N_a S_\rho(f)/\bar{\rho}^2]$  and, curve  $b$ ,  $fS_\rho(f)/\langle \delta \rho^2 \rangle$ , both vs  $\log[f/(1 \text{ Hz})]$  for specimen ND-1. The solid lines show the model spectrum (see text).

lines drawn through the two curves are graphs of the theoretical diffusion noise spectrum,  $2P(\theta) - P(2\theta)$ , for a value of  $f_c = 55 \pm 5 \text{ mHz}$ . The characteristic frequency  $f_c$  implies a diffusion coefficient  $D(300 \text{ K}) = (0.7 \pm 0.2) \times 10^{-6} \text{ cm}^2/\text{s}$ , a factor of 10 lower than the  $8 \times 10^{-6} \text{ cm}^2/\text{s}$  found for  $\text{H}^+$  in bulk Nb.<sup>19</sup>

The characteristic frequency  $f_c$  scaled with  $L^{-2}$  as expected for one-dimensional diffusion.<sup>14</sup> Noise spectra were measured from four specimens prepared on the same substrate (N7-2, N7-1, N7-3, and N7-4) with  $L = 20, 40, 150,$  and  $300 \mu\text{m}$ , respectively. Measured noise spectra of the three shortest specimens resembled the model diffusion spectrum with characteristic frequencies  $f_c = 65 \pm 15, 18 \pm 5,$  and  $3 \pm 2 \text{ mHz}$ , respectively. The noise spectrum of the longest specimen varied as  $f^{-3/2}$  down to the lowest frequency measured (20 mHz). The dependence of  $f_c$  on  $L$  is consistent with  $f_c = D/\pi L^2$  for  $D(300 \text{ K}) = (0.7 \pm 0.2) \times 10^{-6} \text{ cm}^2/\text{s}$ . The variances of the noise of the three shortest specimens each give  $c_0 \approx 0.3 \text{ at.}\%$ .<sup>18</sup>

Normalized noise spectra  $fS_\rho(f, T)/\langle \delta \rho^2(T) \rangle$  were found to depend on  $f$  and  $T$  only through  $f/f_c(T)$ , as expected for diffusion noise. Noise spectra from specimen N7-2 were measured at five temperatures  $262 \text{ K} \leq T_j \leq 369 \text{ K}$ . Plots of  $fS_\rho(f, T_j)/\langle \delta \rho^2(T_j) \rangle$  vs  $\log[f/(1 \text{ Hz})]$  for the five temperatures had the same form;  $f_c(T_j)$  were determined by horizontal translation. Plots of  $fS_\rho(f, T_j)/\langle \delta \rho^2(T_j) \rangle$  vs  $\log[f/f_c(T_j)]$  for the five temperatures (each with a different symbol) are shown in Fig. 3. The indistinguishable superposition of the scaled data is strong evidence for the diffusion process. The small discrepancy with the model calculation (solid line) shows the imperfection of our simple one-dimensional diffusion model. A semilogarithmic plot of  $f_c(T)$  vs  $1/T$  (tabulated in

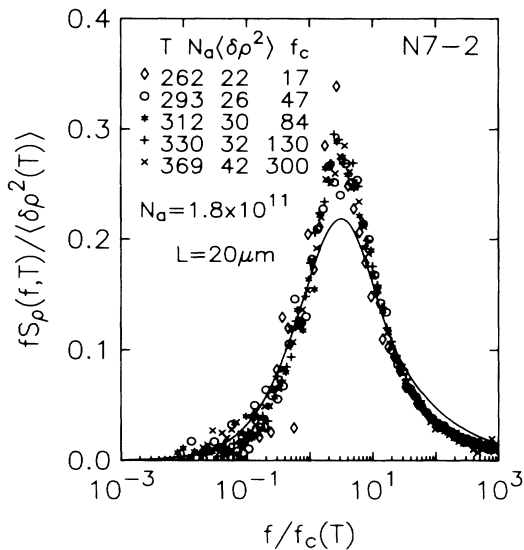


FIG. 3. Plots of  $fS_\rho(f, T)/\langle \delta\rho^2(T) \rangle$  vs  $\log[f/f_c(T)]$  for specimen N7-2. A different symbol is used for each of the five temperatures. For clarity only  $\frac{1}{5}$  of the points are plotted. The solid line is the model spectrum (see text). Tabulated values of  $T$ ,  $N_a(\delta\rho^2)$ , and  $f_c$  have units of K,  $(\mu\Omega \text{ cm})^2$ , and mHz, respectively.

the figure inset) gives a straight line consistent with  $D(T) = D_0 e^{-E/kT}$ ,  $D_0 = (6 \pm 2) \times 10^{-3} \text{ cm}^2/\text{s}$ , and  $E = 230 \pm 10 \text{ meV}$ ;  $E$  is higher than that found for bulk niobium,  $E_0 \approx 107 \text{ meV}$ .<sup>19</sup>

Evanescent trapping of hydrogen by impurities and other defects is known to lower the diffusion rate and increase its effective activation energy in bulk Nb.<sup>20</sup> Oxygen and nitrogen impurities in niobium trap hydrogen with binding energies  $E_b$  on the order of 100 meV. The magnitude of the residual resistivity of our niobium films suggests a defect concentration of 1–3 at.%. Most of the  $c_0 \approx 0.3$  at.% hydrogen in specimen N7-2 would be trapped by such a defect concentration, so that the apparent activation energy for diffusion  $E$  would approach  $E_0 + E_b$ , where  $E_0 = 107 \text{ meV}$  is the activation energy for diffusion of hydrogen in the absence of traps.<sup>21</sup> The effect would be less when  $c_0$  exceeds the trap concentration, since then only a fraction of the hydrogen ions would experience trapping. This is consistent with measurement of  $D(T)$  for specimen N6-1 ( $c_0 \approx 7$  at.%); in this case  $D(300 \text{ K}) \approx 3 \times 10^{-6} \text{ cm}^2/\text{s}$  and  $E \approx 180 \text{ meV}$ . After removal of much of the hydrogen by electrotransport,  $D(300 \text{ K})$  noticeably decreased to less than  $2 \times 10^{-6} \text{ cm}^2/\text{s}$  (see Fig. 2 of Ref. 14).

The diffusion dynamics are altered if defects, say grain boundaries, act as sources and sinks or if precipitation of NbH ( $\beta$  phase) occurs. Formation of NbH may also modify the temperature dependence of

$\langle \delta\rho^2(T) \rangle$ . Noise spectra from some specimens show a knee above 1 Hz that is not accounted for by our simple diffusion model and may be associated with internal sources and sinks.

Additional experiments establish chemical and sputter etching as the origin of the  $\text{H}^+$ . After a specimen is heated in a vacuum (to evaporate hydrogen), its excess noise decreases by two to three orders of magnitude. The residual excess-noise level is then more than an order of magnitude lower than is typically reported for other metals.<sup>12,13</sup> Discussion of this result is deferred to a future publication. Similar decreases occur after a direct current is used to sweep mobile charged defects from the conductor into one of its contact pads. In this case the effect is reversible (favoring  $\text{H}^+$  over other defects) and is accompanied by a resistivity change  $\Delta\rho$  consistent with the noise magnitude.<sup>18</sup> The opposite occurs when the surface of the contact pads are sputter etched (see Ref. 14); the noise and resistivity increases indicate charging with  $\text{H}^+$ . Exposure of one specimen to concentrated HF for 3 min generated excess noise nearly two orders of magnitude higher than a similar untreated specimen. After 15 min in HF, another Nb film cracked and flaked off its substrate, as expected from the large strains induced by hydride precipitation.

It is not surprising that chemical etching would load the films with some hydrogen; hydrogen is commonly loaded into bulk Nb electrolytically with acid solutions or into Nb powders by soaking in concentrated Hf.<sup>22</sup> We think that ion milling introduces hydrogen into the niobium by exposing an oxide-free niobium surface to residual water vapor within the system. This condition is known to form  $\text{H}^+$  and niobium oxide on bulk Nb. Hydrogen diffuses into the thickness of the film faster than the Nb is sputtered away and where sputtered may quickly reach the solubility limit, but it diffuses slowly along the film. This accounts for low  $c_0$  from patterning and large  $c_0$  buildup if the surfaces of the large contact pads are milled.

The scaling of  $S_\rho$  with  $c_0$ ,  $L$ ,  $f$ , and  $T$  identifies diffusion-controlled fluctuations of the number of electron scatterers as the noise-producing mechanism in these Nb films; the observed spectrum is well approximated by a simple one-dimensional diffusion model with open boundaries only at ends of the film segments, thus reflecting the impermeability of the oxide-coated Nb surface to  $\text{H}^+$ . The noise magnitudes, changes in resistivity, values of apparent diffusion coefficients, and the results of charging and annealing experiments implicate hydrogen as the diffusible scatterer, with its diffusion slowed by binding to film impurities. The fluctuation spectra obey a scaling law  $fS_V(f)/\langle [\delta V(T)]^2 \rangle = g(f/f_c(T))$ , where  $f_c$  is a characteristic frequency, here  $f_c = D/\pi L^2$ . This is the first unequivocal identification of an excess low-

frequency noise mechanism in metal films near ambient temperatures.

These first measurements of hydrogen diffusion in sputtered Nb films suggest that resistance fluctuation spectra should be useful for studying hydrogen diffusion in other metal films since both  $D$  and  $c_0$  are determined from  $S_\rho(f)$ . Other perturbations such as defect interactions and hydride precipitation are also reflected in the fluctuation spectra. The large surface-to-volume ratios, defect, and impurity concentrations in metal films make it difficult to study diffusion by the usual methods.

The levels of  $1/f$  noise predicted for Nb films by the customary empirical formulas<sup>12,13</sup> are, respectively, two and one order of magnitude higher than we observed in films with the lowest hydrogen concentration. Hydrogen concentrations  $c_0 \approx 0.1$  at.% generate scattering fluctuation noise comparable with Hooge's empirical value. The noise power due to independent scatterer fluctuations is inversely proportional to the number of scatterers  $N_0$  and proportional to  $\rho_0^2$  for scatterers that obey Matthiessen's rule; thus  $S_\rho(f) \approx \rho_0^2/N_0$ . In contrast, the usual models assumed for  $1/f$  noise have  $S_\rho(f) \propto \bar{\rho}^2/N$ , where  $N$  is either the number of carriers  $N_c$  or the number of atoms  $N_a$  in the conductor.

We find that the temperature dependence of the scaled spectrum of scatterer noise  $N_0(T)S_\rho(f,T)/\rho_0^2(T)$  may be represented by a superposition of Lorentzian spectra with relaxation times  $\tau = \tau_0 e^{E/kT}$  arising from a single activation energy  $E$  and a distribution of prefactors  $\tau_0 = (D_0 k^2)^{-1}$  determined by the specimen geometry. In contrast, the Dutta-Horn model for  $1/f$  noise represents  $N_a S_\rho(f,T)/\bar{\rho}^2(T)$  by a superposition of Lorentzians with a distribution of activation energies  $E$  and a single  $\tau_0$ .<sup>13</sup>

Since scattering strengths for various dissolved impurities and point defects vary by less than an order of magnitude similar noise levels might be generated by other defects and impurities at corresponding spectra regions. However, the diffusion noise spectrum depends on the distribution of  $\tau_0 = (D_0 k^2)^{-1}$  determined by the geometry and the value of  $D$ .<sup>23</sup> Other impurities and defects diffuse sufficiently slowly at ambient temperatures that only reorientation or local reformation at atomic scale distances should be fast enough to generate resistance fluctuations at the usual experimental frequencies. In contrast with  $1/f$  noise, the characteristic feature in our noise spectrum combines with independent observables to identify the underlying physical mechanism. It may be that other mechanisms capable of generating  $1/f$  noise will continue to elude identification until they can be experimentally isolated so as to reveal their characteristic spectra.<sup>6,24</sup>

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