Stress and Silicon Nitride: A Crack in the Universal Dissipation of Glasses

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High-stress silicon nitride microresonators exhibit a remarkable room temperature Q factor that even exceeds that of single crystal silicon. A study of the temperature dependent variation of the Q of a 255 μm $\times$ 255 μm $\times$ 30 nm thick high-stress Si_3N_4 membrane reveals that the dissipation Q^{-1} decreases with lower temperatures and is $\simeq$3 orders of magnitude smaller than the universal behavior. Stress-relieved cantilevers fabricated from the same material show a Q that is more consistent with typical disordered materials. *e*-beam and x-ray studies of the nitride film's structure reveal characteristics consistent with a disordered state. Thus, it is shown that stress alters the Q^{-1}, violating the universality of dissipation in disordered materials in a self-supporting structure.

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Amorphous solids are by nature diverse in composition. Yet it is evident that there is a commonality to their low-energy vibrational spectrum as characterized by a universal dissipation Q^{-1} that "plateaus" as the temperature is varied between roughly 0.1 and 10 K at $1.5 \times 10^{-4} \leq Q^{-1} \leq 1.5 \times 10^{-3}$. The universality of glass was first noted by Zeller and Pohl [1]. The qualitative universality of glasses has been rather successfully explained in terms of the phenomenological tunneling model (TM) [2,3], which assumes the presence of atomic tunneling entities with a broad distribution of energy splittings. The TM does not specify the identity of the tunneling entities, nor does it account for the quantitative universality of glassy properties noted in [4].

In this Letter we describe temperature dependent measurements of dissipation Q^{-1} in high-stress self-supporting membranes and companion stress-relieved cantilevers resonated at their fundamental modes of excitation, and fabricated from silicon nitride, a disordered solid. While the former exhibit an internal friction that is 3 orders of magnitude below that of glassy systems (and within an order of magnitude of a bulk Si single crystal "paddle" resonator [5]), the stress-relieved cantilevers exhibit Q^{-1} close to values observed in glasses. The only other instances where an amorphous solid has demonstrated significant departure from the universal behavior were in hydrogenated amorphous silicon deposited by hot wire chemical vapor deposition (HWCVD) on single crystal silicon [5] (Q^{-1} was 200× smaller), and in other silicon nitride films also deposited on a silicon oscillator [6]. A larger silicon nitride membrane ($f_0 = 135$ kHz) exhibited comparable Q at 297 K [7], and high-stress metallized silicon nitride "nanostring" resonators with comparable Q to those measured in our laboratory at room temperature [8] were described by Schwab [9]. There are no reports of the temperature dependence of bare self-supporting materials that reveal departures from the universal behavior until this work. No convincing quantitative explanation has been forthcoming in the intervening period of more than a decade since the initial publication [5].

There have been many attempts to question the underpinnings of the tunneling model itself. The issue of whether interactions between two-level systems (TLS) play a role in the universality was raised by Yu and Leggett [10], and later by Burin and Kagan [11] and Kühn [12]. It was not until very recently that evidence for the contribution of interactions to Q^{-1} was reported in the literature [13], though there had been earlier reports of anomalous dissipation [14]. This evidence for interactions was only observed well below the universal plateau region. There has been other evidence for interactions between the tunneling entities in the dielectric behavior [15,16]. These results were understood in terms of a hole in the distribution of TLS at zero local field (the "dipole gap") [17,18]. In [19], the dipole gap theory was reconciled with acoustic measurements by noting that the effective range of TLS interactions increases as temperature decreases. Interactions are also cited as contributing to anomalous magnetic field dependent tunneling in glasses [20–22].

The preparation of the Si_3N_4 film is germane to the properties realized. Standard (stoichiometric) silicon nitride is deposited by low pressure chemical vapor deposition (LPCVD) at 775 °C in a 200 mTorr N_2 atmosphere. Once the temperature and pressure are stabilized, a 2-min flow at 196 sccm (standard cm^3/min) of ammonia is initiated, and a dichlorosilane flow at 60 sccm is maintained for the duration of the deposition. On completion of the deposition the dichlorosilane flow is turned off while ammonia flows for 2 min to react with any residual dichlorosilane. The process results in a high-quality silicon nitride film incorporating an included tensile stress (measured with a wafer-bow technique) of 1.20 ± 0.05 GPa that is about 0.63% of the bulk modulus [23]. The conditions are critical since low-stress nitride deposition takes place at 800 °C and 200 mTorr, while dichlorosilane and ammonia flows are 126 and 22 sccm, respectively. The higher dichlorosilane flow creates a silicon-rich nitride that alleviates film stress. In contrast, other processes [24] produce high-stress nitride that dissolves in the HF wet etch used to release the resonator.

In our laboratory we have shown that room temperature mechanical measurements on high-stress nitride exhibit a range of Q values depending on the geometrical configuration and size of the structure [8,25]. We also demonstrated that, in a given device, the mechanical distortion (bending) of the handle wafer supporting a film of low-stress silicon nitride led to the enhancement of the film's Q [26]. It is well known that metallization increases Q^{-1}; therefore, we developed a large scale nonmetallized structure to facilitate the optical detection of resonant motion at low temperatures. The 110 nm-thick Si_3N_4 film was patterned with a 50×50 array of 0.8 μm holes spaced 5 μm apart. The holes admit HF to etch away the underlying 630 nm sacrificial oxide layer, yielding a 255 $\mu\mathrm{m} \times$ 255 μm freestanding resonator attached to the wafer only around the periphery. The resonator's average thickness was reduced to $\sim$30 nm by the etch (estimate based on an observed 14 nm/min Si_3N_4 HF etch rate). The resonator is driven at its fundamental "drumhead" resonant frequency [27] around 1.5 MHz using a piezodisc that vibrates the chip in the out-of-plane direction. To elucidate the role of stress on the dissipation, we also fabricated a silicon nitride cantilever resonator, which, because it is unsupported on three sides, has minimal included stress. The membrane resonator, together with a stress-relieved cantilever, is shown in Fig. 1.

The devices' motion was detected optically [28] on a modified Attocube cryostat [29] operated in vacuum. 785 nm laser light was coupled to a low temperature objective lens via a single mode fiber and was reflected from the resonator-substrate assembly, the light collected and coupled to a photodiode connected to the input of a swept frequency network analyzer. The device and substrate comprise a Fabry-Perot interferometer. The motion of the resonator modulates the intensity of the reflected light. The resonant frequency f_0 of the structures (dictated by a combination of geometry, elastic properties of the material, and temperature dependent stress) was used as an internal thermometer to ensure that heating by the laser (or drive) was not significant. Because the differential expansion between the silicon handle wafer and the nitride dominates changes in the resonant frequency, we do not plot the temperature dependence here.

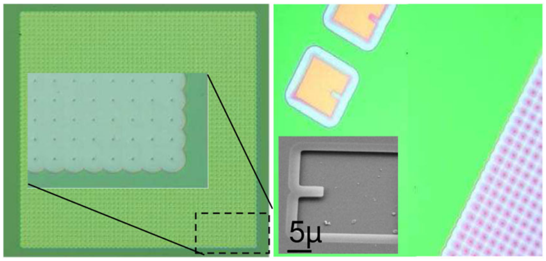

FIG. 1 (color online). Left: Image of a 255 $\mu\mathrm{m} \times 255$ $\mu\mathrm{m} \times$ 30 nm thick silicon nitride resonator (the lighter region). Inset: A corner with 40 of the 50×50 0.8 μm diameter holes required to etch away the underlying SiO_2. Right: A stress-relieved cantilever near a 255 μm square resonator. An identical structure at the top is stuck to the underlying silicon and appears discolored. Inset: An electron micrograph of a similar cantilever.

A single chip had identical resonators fabricated adjacent to one another. In a 3×3 array, all resonators exhibit $Q^{-1} \simeq 10^{-6}$ at room temperature with the exception of one structure with a Q ($\approx 10^4$) possibly due to a crack. The Q and f_0 were obtained by fitting the response of the resonator to a Lorentzian, and the Q was determined from the half-power width, Δf ($Q = f_0/\Delta f$). The resonators were driven at a small enough amplitude (estimated to be $\approx$1 nm) to maintain a linear response (Lorentzian line shape and negligible frequency shift with amplitude). The response of membrane and cantilever resonators is shown in Fig. 2.

The temperature dependence of the internal friction, along with typical values observed for crystalline silicon and amorphous SiO_2 [6], is plotted in Fig. 3. At room temperature the internal friction of the Si_3N_4 resonator is lower than that measured for silicon double-paddle resonators (solid red line in Fig. 3), but the approximately 2 orders of magnitude decrease in Q^{-1} of the Si as the temperature is lowered is not observed in the glassy resonator. The contrast with the behavior expected for glasses is all the more striking with the high-stress nitride displaying a 3 orders of magnitude lower dissipation than SiO_2.

The temperature dependent dissipation of the stress-relieved cantilevers is plotted in Fig. 3 and is below the band of values seen in glasses (blue bar) by approximately a factor of 2. Thus, it is clear that the dissipation of the LPCVD stress-relieved film is more consistent with typical glassy behavior and is within an order of magnitude of results reported by Liu *et al.* [6].

In order to verify that the silicon nitride material is disordered, we examined an unreleased high-stress sample grown in the same batch. X-ray diffraction scans taken using a Scintag ID3000 spectrometer and general area detector diffraction system (GADDS) show a broad flat scattering region below 20°, the result of diffraction from an amorphous material in contrast to peaks which would be

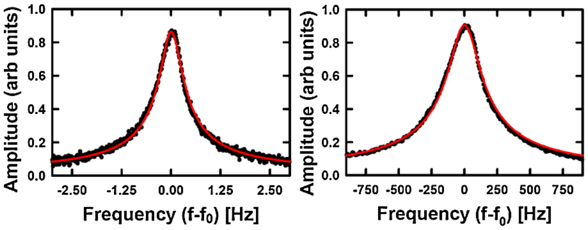

FIG. 2 (color online). The amplitude response (points) and fits (solid lines) for a high-stress membrane (left, $f_0 =$ 1.526 445 MHz, $Q = 2.68 \times 10^6$) at 4.76 K, and stress-relieved cantilever resonator (right, $f_0 = 3.538\,700$ MHz, $Q = 1.48 \times 10^4$) at 4.7 K.

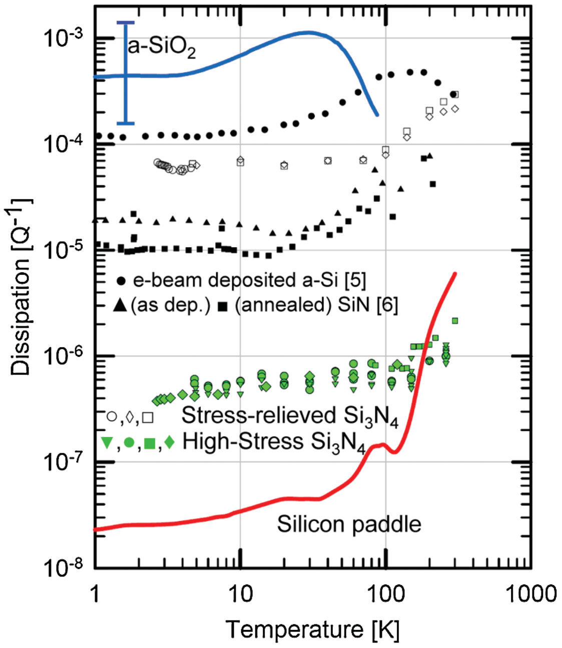

FIG. 3 (color). Temperature dependent internal friction measured for our high-stress LPCVD Si_3N_4 membrane structures. This is contrasted with the behavior of a-SiO_2 (solid blue line) and single crystal Si (solid red line) [5]. The range of "plateau" region values of Q^{-1} for a-SiO_2 is shown by the blue bar. We also show for comparison results for e-beam deposited a-Si [5] and supported LPCVD films of SiN [6]. Our data on cantilever structures fabricated from the same LPCVD film as the high Q membranes show Q^{-1} a factor of ~2 below the lower extent of the band consistent with other glassy materials.

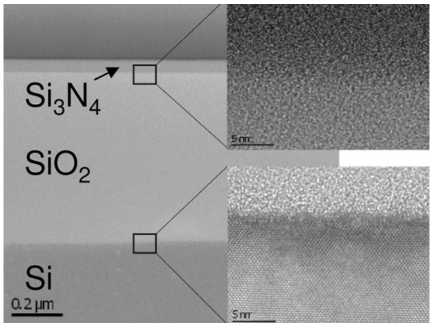

FIG. 4. Top: High resolution TEM images showing no long-range order in the SiO_2 or Si_3N_4 in contrast to the Si lattice.

characteristic of crystalline order. We also obtained TEM images of our $Si_3N_4/SiO_2/Si$ composite structure. These reveal no long-range order: while the lattice in the Si (wafer) is clearly revealed, no such structure is seen from the images captured from the SiO_2 or Si_3N_4 (Fig. 4). This conclusion is supported by conventional e-beam diffraction and convergent beam electron diffraction (CBED). We conclude that the high-stress Si_3N_4 is not crystalline.

According to the tunneling model, the internal friction Q^{-1} of glasses in the plateau region is given by [5]

$$Q^{-1} = \frac{\pi}{2}\frac{\bar{P}\gamma^2}{\rho \nu^2}. \tag{1}$$

$\bar{P}$ is the spectral density of tunneling states, γ is the coupling energy of the tunneling states to the lattice, ρ is the mass density, and ν the sound velocity. This expression (and the TM) are strictly applicable below 1 K where thermally activated reorientations of the tunneling entities are negligible. Nevertheless, it is a general experimental observation that the "plateau" extends to 5 K for a wide range of materials and frequencies [30].

It is clear from our results that stress and not hydrogen content is the origin of the anomalously low Q^{-1} that we observe in high-stress silicon nitride. Liu and coauthors observed a much lower dissipation in HWCVD a-Si than in e-beam deposited a-Si and Si+ implanted a-Si [5] and attributed this difference to the hydrogen incorporated in the a-Si films by the HWCVD process. This added hydrogen results in a Q^{-1} comparable to those seen in our high-stress silicon nitride resonators. It was conjectured that the hydrogen might lead to the formation of an amorphous network with more perfect fourfold coordination [5]. As noted in one of the original tunneling model papers, the high coordination number that accompanies tetrahedral bonding is expected to inhibit the tunneling process, thus decreasing the density of tunneling states [3]. However, fourfold coordination does not guarantee low Q^{-1} [31]. Silicon nitride also has fourfold coordination and is a candidate for a correspondingly lower dissipation at the plateau. We compare resonators fabricated from identical films, with similar chemical composition [32] and coordination number, with stress being the sole distinguishing factor. Thus hydrogen or coordination number alone cannot be responsible for the anomalously low dissipation observed in the high-stress material. Regardless of the origin, one comes to the conclusion that either the spectral density $\bar{P}$ or the coupling energy γ must be radically altered by the application of stress.

We offer the following conjectures that would have to be tested. We note that all of the films considered here (in our lab and elsewhere) range from 30 nm to 2 μm thick; thus they have enhanced surface to volume ratios compared to conventional macroscopic resonators. At first sight, the quasi-two-dimensional nature of the structures should be important since the availability of nearby sites for tunneling would be different for surface atoms. Yet it was shown in [33] that the Q^{-1} plateau levels in a-SiO_2 films as thin as 0.75 nm are nearly the same as in bulk a-SiO_2 (while Q^{-1} at $T > 10$ K was modified from bulk). So surfaces alone do not alter Q^{-1}. An understanding of the effect of stress could come from two-site models where it is thought that most of the tunneling entities reside on *internal* surfaces (nanovoids) in the glass [34,35]. Such nanovoids' contours might be more distorted by stress, affecting the tunneling between nearby sites.

The second conjecture relates to the significant departures from the accepted "universal" behavior seen by Liu and co-workers [5,6] in thin film materials deposited onto a bulk Si substrate. Since the thermal expansion relative to deposition temperature is likely to be different in the film and in the Si/SiO_2 underlayer, the result is either tensile or compressive stress in the film, both of which can lead to higher Q [26,36]. If this conjecture is correct, then the source of the departure from universal behavior in all of these (few) cases can be traced to the presence of stress. Assuming a flat distribution of $\bar{P}$, $\gamma = 1$ eV, a small static strain would not affect Q^{-1} since it would simply perturb the asymmetry of a tunneling state by an amount $\sim$1 eV × strain. However, in high-stress nitride, the strain (= stress/bulk modulus) ~ 0.007. Thus the strain energy is of order 70 K. The plateau in Q^{-1}, the linear heat capacity, and the quadratic thermal conductivity all set in below 10 K. Thus it is possible that by applying strain a significantly altered region of the distribution is being accessed.

Regardless of the origin of these effects, whether due to sensitivity of the spectral density or the coupling energy to stress, or because of the effect of stress on tunneling entities confined to surfaces in the form of nanovoids, it is obvious that further work is needed to determine the origin of this nonuniversal behavior. An important question is whether similar stress-sensitive changes will be seen in conventional glassy materials, especially in the related dielectric properties. Will the hallmarks of universal glassy behavior, the T-linear specific heat and T^2 thermal conductivity [1], be observed in high-stress Si_3N_4 and are these quantities affected by stress? We also hope that this result provokes new experimental and theoretical efforts aimed toward understanding the effect of stress on dissipative processes in glass.

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