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Low Temperature Mechanical Properties of Boron-Doped Silicon

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The audio-frequency mechanical properties of oscillators fabricated from boron-doped single-crystal silicon were measured as a function of temperature. The mechanical properties (Q^{-1} and period) are dominated by the boron impurities and cannot be attributed to glassy defects. We also found the higher strain mechanical response of these crystals to be nonlinear below 0.3 K. The strength of this nonlinearity is related to the boron concentration.

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The low temperature mechanical properties of silicon have been explored most recently by Kleiman, Agnolet, and Bishop (KAB) [1], who observed anomalous behavior in the dissipation and frequency of audio-frequency modes of their mechanical oscillators. This behavior was attributed to the presence of glassy tunneling defects which they postulated to be intrinsic to silicon. The concentration of such glassy defects was estimated from the data as about 5×10^{16} cm^{-3}, about 1% of that found in vitreous silica [2]. The existence of glassy defects would be significant, having consequences for the standard model of glasses and for the performance of silicon in bolometric neutrino detectors [3]. However, two alternative mechanisms have subsequently been proposed. Phillips [4] showed how tunneling states, with nonglassy distributions of parameters, would reproduce the dissipation features observed by KAB at a defect concentration of 10^{14} cm^{-3}. Keyes [5] pointed out that a concentration of 3×10^{12} cm^{-3} localized charges occupying energy-split ground states could explain the normalized frequency shift data of KAB.

Electronic states as proposed by Keyes are known to exist [6] at low temperatures in the bound hole states of acceptor impurities in semiconductors. Such hole states scatter phonons very strongly, as is manifested in thermal conductivity [7] and ultrasonic attenuation measurements [8]. We have carried out a systematic survey of the mechanical response of oscillators similar to those employed by KAB in order to explore the possible importance of this mechanism and allow comparison to the data of KAB. The oscillators were fabricated from uncompensated silicon wafers [9] with boron concentrations of 6×10^{13}, 1.4×10^{15}, 1.1×10^{16}, and 5.7×10^{16} cm^{-3} corresponding to room-temperature resistivities of 200, 7, 1, and 0.2 Ω cm, respectively. The concentrations of the most abundant nonelectronic impurities, oxygen and carbon, were measured using secondary-ion-mass-spectrometry analysis to be 10^{18} and 4×10^{16} cm^{-3}, respectively.

In this Letter, we report results which demonstrate that the mechanical properties of our oscillators are strongly affected by the presence of electronic holes occupying energy-split ground states. Furthermore, the mechanical response of our lowest dopant oscillator suggests that large concentrations of glassy states (as estimated by KAB) are not intrinsic to silicon. We also observed previously unexamined nonlinear response at higher strains. This nonlinearity is less pronounced at higher temperatures, and its low temperature strength increases with doping level.

The oscillators were fabricated from commercial wafers, two-side polished and of (100) orientation. The wafers were machined into double-paddle oscillators using photolithographic patterning and anisotropic etching [10]. Our wafer orientation is different from that of KAB because post-etch corners for (100) wafers are geometrically regular, while those of the (110) wafers used by KAB are not [11]. The samples were cooled to dilution refrigerator temperatures and their response measured while operating the oscillators in their high-Q torsion mode. This mode corresponds to the oscillator head twisting out of phase with the more massive oscillator paddles. Three of the oscillators were made from 200-μm-thick wafers, with the frequency of this mode being between 3.4 and 3.6 kHz, while the other oscillator (7 Ω cm) was fabricated from a 450-μm-thick wafer and operated at 10.7 kHz.

The low-strain response [12] taken at constant amplitude is shown in Figs. 1(a) and 1(b). In Fig. 1(a), we plot the Q^{-1} of the four silicon oscillators. For the oscillators with the three highest doping levels, the dissipation exhibits a strong temperature dependence below 1 K. The loss passes through a maximum near 70 mK for the two oscillators with the highest doping levels, and near 100 mK for the 7-Ω cm oscillator, and then falls rapidly for temperatures below that of the peak. This maximum in the dissipation increases with doping level. No such maximum is observed for the 200-Ω cm sample. Instead, we observe a dissipation plateau from 1 to 0.1 K, below which the loss falls with temperature.

We also have measured the behavior of the elastic modulus which is manifested in the resonant period P. The period of the torsion pendulum, normalized to P_0 (the value near 1 K), is shown in Fig. 1(b). The period change is always positive; the crystal shows softening at all temperatures below 1 K for all the samples measured. Once again, the magnitude of the period change over these temperatures increases with doping level. In addition, we have measured the period change for the two

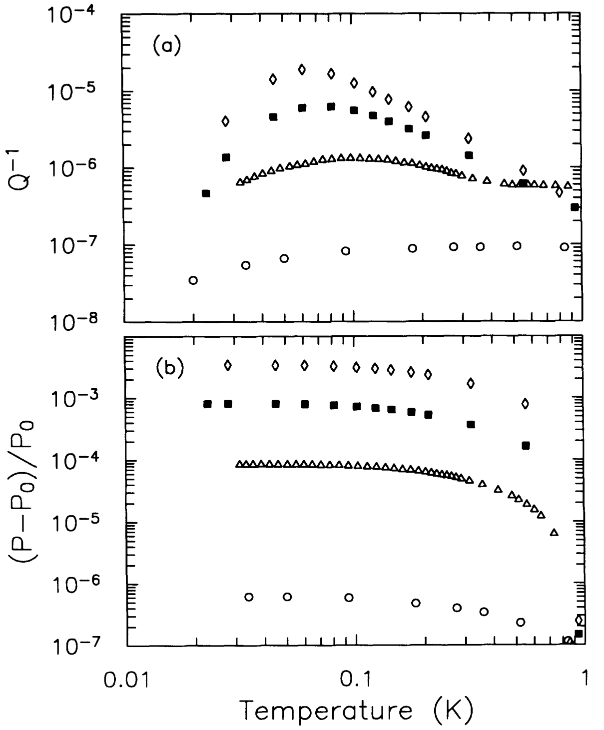

FIG. 1. (a) The dissipation and (b) period change for the four doped silicon oscillators: 0.2 Ω cm (◇), 1.0 Ω cm (■), 7 Ω cm (△), and 200 Ω cm (○). The dissipation and period change relative to 1 K show systematic increases with doping level.

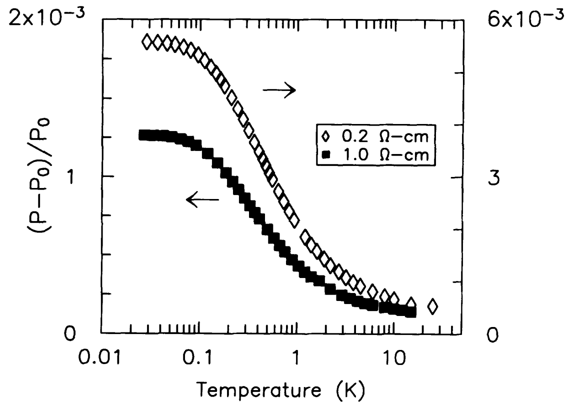

FIG. 2. The temperature dependence of the resonant period change at temperatures up to 20 K for the 0.2-Ω cm (◇) and 1.0-Ω cm (■) oscillators. The data show a log$T$ dependence of the period change below ~1 K, and the onset of crystal softening below ~10 K.

higher doping level oscillators to a temperature of 20 K. As shown in Fig. 2 the period change shows a log$T$ dependence to 1 K, and then saturates near 10 K.

The period change data of the three highest doping density oscillators are consistently explained, using the analysis of Keyes [5], as scattering of the acoustic waves generated by the oscillator vibrations from the boron hole states. Low temperature softening of the crystal is characteristic of localized charges occupying energy-split ground states. The presence of the softening to 10 K suggests there is a distribution of energy splittings. Consider a distribution of splittings which is constant for energies from $-U$ to U, and zero for other energies. A concentration of N_a holes with such a rectangular splitting distribution will cause a period change given by $(P-P_0)/P_0 = D^2(N_a/3U)(1/c_{44})$, where D is an elastic coupling constant and c_{44} the shear elastic constant. The distribution width is given by the temperature range over which the period change shows a log$T$ dependence, here ~1 K. The measured period change is consistent with this width for a coupling constant of 3 eV, similar to values obtained elsewhere [8,13].

Further evidence of the importance of boron holes comes from consideration of the dissipation data of the three highest dopant oscillators. The loss of acoustic waves scattered from acceptor impurities has been calculated by Isawa, Takeuti, and Mikoshiba [14]. Fits to our data indicate that the low energy splittings are particularly important and have characteristic energies corresponding to a temperature of 0.1–0.2 K. Calculation shows that the contribution to the dissipation falls rapidly for splittings above 0.2 K. Thus, the dissipation data cannot provide detailed information on the splitting distribution.

Thus, both the period change and dissipation are dominated by the electronic holes. The period data also indicate an energy-splitting distribution of width 1 K. This distribution is consistent with one arising from the elastic strains from our oxygen impurities [15]. However, this question is the subject of ongoing investigations which will examine samples of different oxygen concentrations.

The mechanical properties of our highest dopant oscillators are very different from the doped samples studied by KAB. Most striking is the absence in the KAB oscillators of a prominent dissipation peak. This difference most likely originates from the nature of dopants they used. The KAB doped oscillators were made from a 0.3-Ω cm As-doped wafer, a 20-Ω cm P-doped wafer, and a 40-Ω cm B-doped wafer. Their two highest doping level oscillators, then, contained *donor* impurities. The bound electrons of donor impurities scatter sound waves much more weakly than bound holes of acceptors due to the chemical shift splitting of order 10 K. Their only acceptor impurity oscillator was doped to a concentration too small to allow observation of a dissipation peak above the "background" dissipation of their undoped sample.

Comparison of our 200-Ω cm oscillator with the KAB high purity oscillator suggests that glassy states are not intrinsic to silicon. Our 200-Ω cm oscillator exhibits a dissipation 10 times smaller than that of the KAB high purity oscillator. Since the dissipation is proportional to the density of states, this would imply that our sample has a concentration of glassy sites 10 times smaller than found in the KAB sample. This is unlikely, since our sample has much higher concentrations of both electronic and nonelectronic impurities. We conclude that such states are not intrinsic to silicon. This conclusion was suggested in the low dissipation measured for a large bar silicon oscillator [16] studied above 1 K. Our data, taken at low temperatures using the paddle oscillator, provide conclusive evidence. The higher dissipation observed by KAB may originate in defects associated with strained torsion rod corners, and this question is currently under investigation.

We have also studied the response of our oscillators to strain levels higher than 10^{-6} by measuring their resonance curves. Each oscillator was driven by a synthesizer whose sine wave frequency at a fixed amplitude was stepped through mode resonance. The frequency was changed in 1-μHz steps. The time between frequency steps was small enough that the response did not lag, and this time was scaled with the oscillator Q. At the time steps employed here, it took 12 h to measure the resonance curve at one drive level.

The resonance curves for the 1-Ω cm sample, taken while increasing the drive frequency, are shown in Figs. 3(a) and 3(b). A temperature dependence in the high strain response is evident in Fig. 3(a). The resonance curve at 322 mK is symmetric, and is well described by the Lorentzian characteristic of linear response. As the oscillator is cooled, the resonance curves become increasingly asymmetric, with the curve peak being pulled toward higher frequencies. The features of this increased nonlinear response at low temperatures are shown in more detail in Fig. 3(b). The highest drive curve shows a jump down in the response amplitude. Sweeping downward in frequency, the oscillator shows hysteretic response (which indicates the effect is not self-heating). This oscillator, then, displays nonlinear response which is less pronounced at temperatures above 0.3 K. Such behavior has been observed for all our oscillators.

We have quantified this nonlinearity in terms of the shift of the resonant frequency. We find the resonant frequency shift to be quadratic in the response amplitude a, so that $\omega_r=\omega_0+\kappa a^2$, where κ characterizes the size of the nonlinearity. We fitted the measured resonance curve to a curve calculated using the above amplitude-dependent resonant frequency [17]. For drive frequencies near the natural frequency, $\omega_0+\delta$, the amplitude a is given by

$$a^2[(\delta-\kappa a^2)^2+(\omega_0/Q)^2]=(F/I)^2(1/\omega_0)^2,$$

where F is the driving force amplitude and I is the oscillator moment of inertia. As seen in Fig. 3(b), the measured resonance curves (triangles) are well described by such calculated curves (the solid line). The temperature dependence of κ for our two higher doping oscillators, when a is expressed in strain units, is shown in Fig. 4. For both oscillators, the nonlinearity peaks near 70 mK, with a magnitude that increases with doping concentration. Data for the 1.0-Ω cm oscillator suggest that the nonlinearity is always present at low temperatures, and this is confirmed by data for the 7-Ω cm oscillator down to 1 mK.

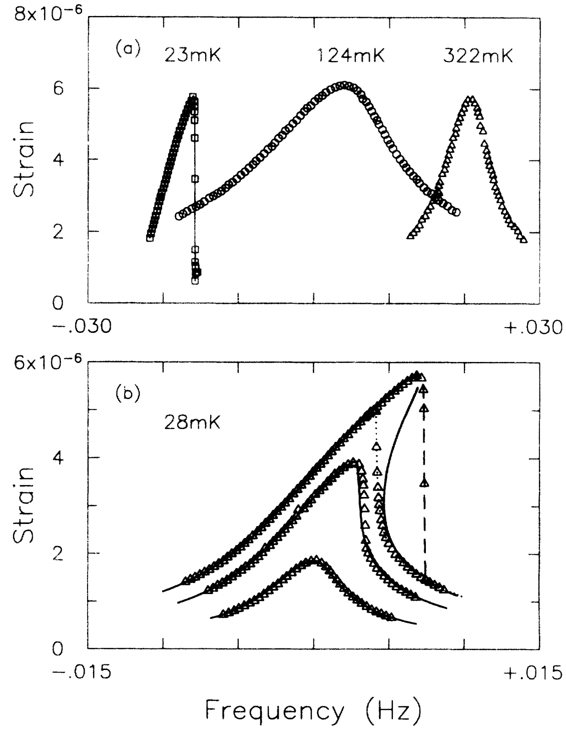

FIG. 3. The nonlinear behavior of the 1-Ω cm oscillator. (a) Resonance curves measured at various temperatures showing a decreased nonlinear response above ~0.3 K. (The line through the 23-mK data is a guide to the eye.) (b) Low temperature resonance curves measured at three different drive levels. The solid lines show resonance curves calculated for peak frequencies given by $\omega=\omega_0+\kappa a^2$, using the same value of κ for all three curves. Also shown is the hysteresis of the highest drive resonance curve. Sweeping up in frequency, the oscillator response follows the dashed line; sweeping down, the response follows the dotted line.

Features of the temperature dependence of κ suggest the nonlinear response is related to the boron hole states. First, the nonlinearity peaks at the temperature of the dissipation maximum for these oscillators. Also, the strength of the nonlinearity, as reflected in κ values, increases with the doping concentration. This implies that the onset strain at which the nonlinear frequency shift is observed decreases as the doping level increases.

The particular mechanism by which the hole states cause the nonlinear response is unknown. The simplest mechanism one can invoke arises when the strain from the applied oscillations is large enough to cause population changes. Such a mechanism would imply that the onset strain for the nonlinear response would be roughly the same among all our samples, due to the similar splitting distributions. Our data, however, show an onset strain that is concentration dependent. The mechanism for the nonlinearity, then, awaits theoretical study.

In summary, we have identified bound holes from ac-

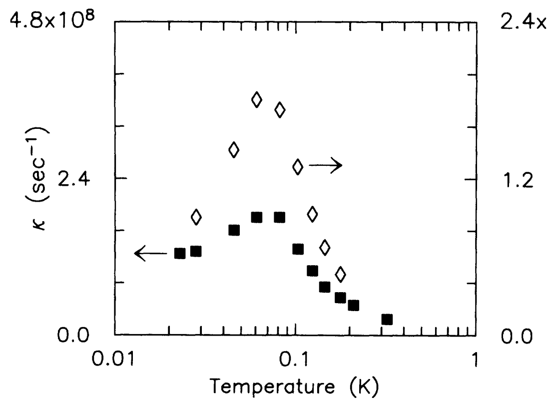

FIG. 4. The temperature dependence of the nonlinearity parameter κ for the 0.2-Ω cm (◇) and 1.0-Ω cm (■) oscillators. For both oscillators κ peaks at the temperature of the dissipation maximum, with the magnitude of κ increasing with doping level. For the 1.0-Ω cm oscillator, κ appears to saturate at low temperatures.

ceptor impurities as strong scatterers of acoustic frequency sound waves. This confirms the importance of small concentrations of localized electronic defects in determining the low-frequency mechanical response of materials. Such scattering was not observed in the earlier work of Kleiman, Agnolet, and Bishop, most likely because of the nature of the samples they studied. Further, consideration of our lowest doping sample suggests that glassy states as proposed by KAB cannot be intrinsic to silicon. We have also observed a nonlinear response that is less pronounced above 0.3 K. Characterizing this nonlinearity by its amplitude-dependent contribution to the resonant frequency, we find the nonlinearity is strongest at the temperature of the dissipation peak, but the mechanism cannot be easily parametrized in terms of theory.

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