Brillouin-scattering measurements of surface-acoustic-wave velocities in silicon at high temperatures

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Brillouin-scattering measurements of the angular dependence of surface-acoustic-wave velocities at high temperatures are reported. The measurements have been performed on the (001) surface of a silicon single crystal at temperatures up to 800°C, allowing comparison of the results with calculated velocities based on existing data for the elastic constants and thermal expansion of silicon in this temperature range. The change in surface-acoustic-wave velocity with temperature is reproduced well, demonstrating the value of this technique for the characterization of the high-temperature elastic properties of opaque materials.

I. INTRODUCTION

There is widespread interest in the elastic properties of solids at elevated temperatures. Much of the impetus for current research in this area has arisen from geophysical and geochemical studies of the earth's mantle[1] and from the need to understand the properties of refractory materials[2] and hard coatings. Elastic constant data at high temperatures are also a valuable source of information on the interatomic potentials used in computational simulations of solids.[3]

Brillouin scattering has proved to be one of the more powerful means for studying the high-temperature elastic properties of transparent materials.[4] The technique requires no mechanical contact and it can be applied to samples as small as 1 mm on edge, as well as to reactive samples, provided that they are sealed in a protective atmosphere.[5] As a result, Brillouin scattering has led to significant progress in our understanding of phase transitions and other physical phenomena.

In the past, Brillouin scattering at high temperatures has to some extent been hampered by the difficulty in dealing with the low signal to noise ratio of opaque samples, and the increase in background blackbody radiation with temperature which tends to swamp the signal. With the advent of the tandem Fabry-Pérot interferometer (TFPI),[6,7] these problems have become more tractable. The exceptional contrast of the instrument allows one to probe the elastic properties of opaque samples through the scattering that occurs at or near the surface, while the elimination of overlapping interference orders greatly reduces the blackbody radiation background.

As a result of these advances, Brillouin scattering is now widely used to study surface excitations in a large variety of opaque materials under ambient conditions.[8,9] In the case of scattering from crystals, quantitative interpretation of the spectra is aided by the existence of analytical techniques for studying surface acoustic waves (SAW's) and pseudosurface acoustic waves (PSAW's) on various crystal planes.[10,11] Despite these technical and theoretical developments, however, the extension of surface Brillouin scattering to high-temperature studies of opaque materials has not been exploited up to now.

In a successful synthesis of the concepts discussed above, we report here high-temperature Brillouin scattering measurements of the angular dependence of the SAW velocity on a crystal surface. The measurements have been performed on the (001) surface of an n-type silicon single crystal at temperatures up to 800 °C. Using existing high-temperature data for the elastic constants[12] and thermal expansion[13] of silicon, we are able to directly compare our measurements with the theoretically predicted angular dependence, using the computational scheme of Farnell.[11]

II. EXPERIMENTAL PROCEDURE

In surface Brillouin scattering from opaque materials, laser light incident on the sample is inelastically scattered by surface acoustic waves through the so-called ripple mechanism.[8] A typical backscattering geometry is illustrated in the inset in Fig. 1. The incident wave vector $\mathbf{k}$ of the light makes an angle θ with the surface normal and the spectrum of the light inelastically scattered back into a small cone around $-\mathbf{k}$ is collected. The SAW amplitude decreases rapidly to zero beneath the surface and so wave-vector conservation is only relevant for the component of $\mathbf{k}$ parallel to the surface. Thus for backscattering from a surface mode with wave vector $\mathbf{K}_{\|}$, we have

$$K_{\|} = 2k\sin\theta.$$

The phase velocity V of the SAW is then related to the spectral frequency shift f_B by

$$V = 2\pi f_B / K_{\|}.$$

In our experiments, the angular dependence of the SAW velocity in the crystal plane is measured by rotating the sample about its surface normal, while keeping θ fixed. In order to satisfy these geometrical requirements,

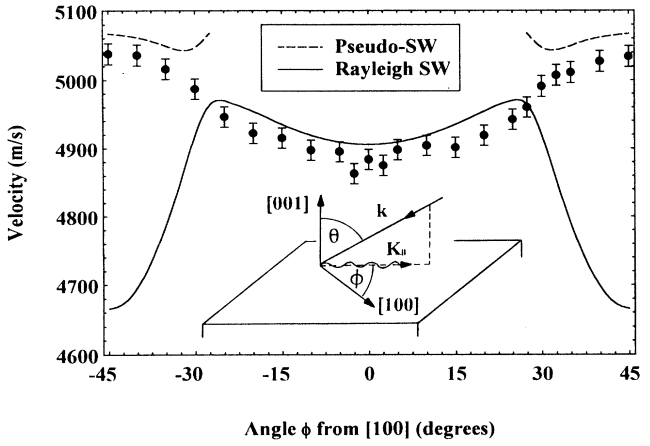

FIG. 1. Measured angular dependence of surface wave velocities at room temperature on (001) n-type silicon, compared to calculated SAW and PSAW velocities. The symmetry of the data allows accurate assignment of the [100] direction in the sample surface.

a specially designed optical furnace with rotatable sample holder was assembled. The measured velocities are fairly sensitive to changes in θ, so this angle must be known with high precision. Using a vernier protractor, a value of $\theta = 70.9(2)°$ was found with the sample in the furnace. This was confirmed using a slightly less accurate optical technique.

The furnace can be adapted to handle encapsulated samples, should the material be too reactive for the furnace environment. Sample temperature was monitored by a platinum-platinum 13% rhodium thermocouple placed immediately next to the sample. A temperature controller was used to maintain thermal stability of better than 1 °C during the rather lengthy measurement series.

A Sandercock (3+3)-pass tandem Fabry-Pérot interferometer, similar to that described in Ref. 7, was used in conjunction with the 514.5-nm line of an argon-ion laser operated in a single mode. Reflection losses of the 140-mW incident beam were reduced by polarizing the beam in the sagittal plane. The scattered light passing through the interferometer was detected by a cooled photomultiplier tube with less than one dark count per second. An acousto-optic modulator was used to protect the photomultiplier tube from the intense elastic peak, thus preventing problems of overload.

In order to illuminate the sample inside the furnace with the laser beam, a 120-mm focal length lens of aperture $f/5.3$ was used. This decreases the count rate, as the solid angle around θ from which backscattered light is collected is fairly small. Nevertheless, the scattered intensity was still sufficient for satisfactory spectra at room temperature. Measurements required progressively less time at higher temperatures, due to the expected linear increase in scattering cross section with temperature.

The small lens aperture does have the advantage of providing good angular resolution by decreasing the collection cone of scattered light. It also goes some way towards solving a problem encountered by Sandercock in his pioneering Brillouin-scattering measurements of angular dependence of SAW velocities in silicon at room temperature,[14] where it was found that the experimental values for velocity were about 2% lower than the calculated ones. The discrepancy can be at least partially explained[15] on the basis that the scattered intensity displays a maximum for $\theta \simeq 60°$ in silicon,[16] whereas the measurements of Sandercock were performed using an angle of incidence of 76° and an $f/1.8$ collection aperture. Thus the line center is displaced from the center of the aperture towards a smaller scattering angle, corresponding to smaller surface phonon wave vectors. Although Elmiger has argued[16] that this explanation is not entirely compelling, the velocities found here do correspond more satisfactorily with the theoretical values.

III. RESULTS AND DISCUSSION

Our SAW velocity data were gathered at 30 °C, 197 °C, 397 °C, 600 °C, and 800 °C. The measurement at 30 °C illustrates the effect of beam heating inside the furnace, as the room temperature was 23.5 °C. During the 800 °C series, the sample started to develop a surface coating, which increased the background due to elastically scattered light. Although further measurements at higher temperatures were precluded, the 800 °C series was successfully completed.

In the (001) plane of a cubic crystal, symmetry dictates that one need only measure the SAW angular dependence over the 45° interval between [100] and [110]. The symmetry directions in the sample were confirmed using Laue x-ray methods, but it was still necessary to accurately align the laser beam with these directions once

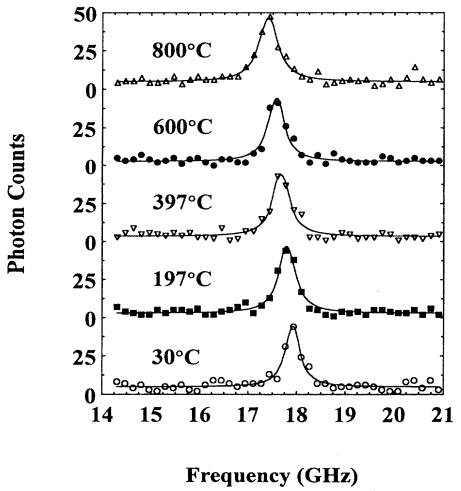

FIG. 2. The anti-Stokes Brillouin-scattering spectra for SAW along [100] in (001) n-type silicon. The gradual decrease in frequency shift with increasing temperature can be seen clearly. The solid curves are least squares fits of the Lorentz distribution to the data. Spectral accumulation times decreased progressively as the scattering cross section increased with temperature.

the sample was inside the furnace. For this reason, an extensive series of measurements was performed with the sample at 30 °C. The results are shown in Fig. 1 in which the expected symmetry is clearly visible. In this way, the [100] direction could be assigned with at least 2° accuracy. The angle ϕ between $\mathbf{K}_{\|}$ and [100] (see Fig. 1) could thereafter be selected with repeatability of 0.1° relative to the furnace housing.

A typical spectrum was subjected to a three point binomial smoothing, before the centers of the Brillouin peaks were found using a peak search function on the multichannel analyzer. A more rigorous approach, involving the least squares fitting of an assumed Lorentz distribution to the raw data, accurately reproduced these peak positions for a representative selection of spectra. The anti-Stokes Brillouin component of the [100] SAW spectra are shown in Fig. 2 for all of the measured temperatures. The solid lines are fits of the Lorentz profile. The error in this peak analysis procedure was estimated to be about 0.3%, which accounts for the observed scatter in the data.

Included in Fig. 1 are the calculated generalized Rayleigh surface wave, as well as the pseudosurface wave which exists near [110]. In the vicinity of [100], only the Rayleigh wave can be observed. As ϕ goes beyond 26° the Rayleigh velocity curve bends over to asymptotically approach the bulk transverse velocity curve, eventually becoming degenerate with it at $\phi = 45°$. This process is accompanied by a loss of normal displacement at the surface and consequently weaker coupling to the light, leading to the disappearance of the Rayleigh signal. For ϕ larger than 30°, it is rather the pseudosurface wave that has the large normal displacement and is thus observed in the Brillouin scattering. In the crossover region between 25° and 30°, we were unable to resolve the individual waves, but have instead observed a slight broadening of the Brillouin peaks, giving the illusion of a smooth transition between the two velocity curves.

All of the calculated curves presented in this paper required data relating to the bulk elastic constants as well as to the density. In order to perform an evaluation of the technique at high temperatures, we have used elastic constant data measured by ultrasonic methods using a single crystal of p-type silicon,[12] and thermal expansion data derived from powder x-ray measurements[13] on pure silicon. These are the only sources covering all of the required temperature range, so we have used their results despite our sample being n-type material. Studies of the influence of the free current carriers on the elastic constants of silicon[17] indicate that there is little effect at impurity concentrations up to 10^{17} cm^{-3}. The concentration of phosphorus in our n-type sample was about 10^{16} cm^{-3}, while the large p-type sample used in the ultrasonic measurements contained some 10^{17}-cm^{-3} impurities. Therefore it appears reasonable to use the two data sets for purposes of comparison and evaluation.

Nevertheless there is a clear trend in Fig. 1 for the experimental points to lie slightly lower than the theoretical curves. This trend was also found for the data at higher temperatures. Taking an average over the data set of Fig. 1, a deviation of 0.53% was found between the

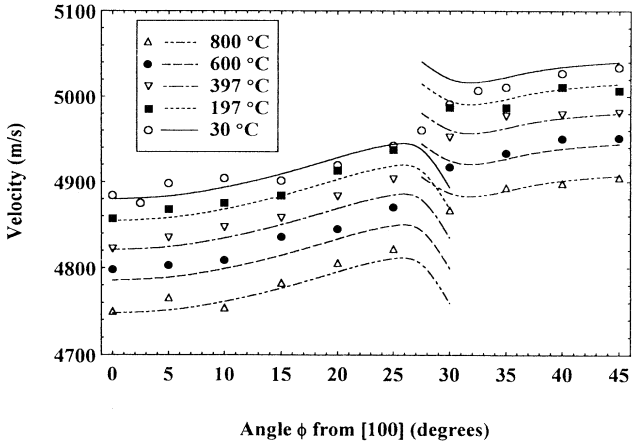

FIG. 3. Brillouin scattering measurements of the temperature dependence of the surface wave velocities in n-type silicon up to 800 °C. The curves are calculated from elastic constants obtained through ultrasonic measurements (Ref. 12) and thermal expansion data (Ref. 13). They have been uniformly decreased by 0.53% in order to emphasize the theoretically predicted changes with temperature.

measurements and calculations. Some part of this error may be due to factors such as the error in θ ($\pm 0.12\%$) and the uncertainty in the calibration of the free spectral range ($\pm 0.2\%$). Both of these sources of error would tend to cause a constant offset for all of the data points. Moreover there might still be some remnant of the aperture shift observed by Sandercock as discussed earlier.

An additional source of discrepancy for surface Brillouin-scattering measurements has been identified in Ref. 18, where a 3% decrease in SAW velocities in nickel was observed. This was attributed to surface damage induced during mechanical polishing and could be corrected to some extent by surface sputtering. The significance of this effect is not clear in the present case, as the final stage of surface preparation for a commercial silicon wafer involves chemical etching.

Any remaining discrepancy can, however, be attributed to the uncertainty in the elastic constants obtained from ultrasonic measurements. If one considers the standard deviation in the mean of all of the available room temperature elastic constants,[19] one finds an average uncertainty of $\pm 0.45\%$ in the calculated surface wave velocities. In combination with the uncertainty in the Brillouin results, this is sufficient to account for the apparent discrepancy.

Our high-temperature measurements of the angular dependence of SAW velocities in the (001) plane of silicon are presented in Fig. 3. For purposes of clarity, the calculated curves in this diagram have been uniformly decreased by a factor of 0.53%. This serves to emphasize the changes in velocity with temperature, rather than the inherent systematic errors in the two data sets. In general the calculated velocities appear to account well for the data. This is further illustrated by Fig. 4 where the experimental and calculated data for [100] are normalized

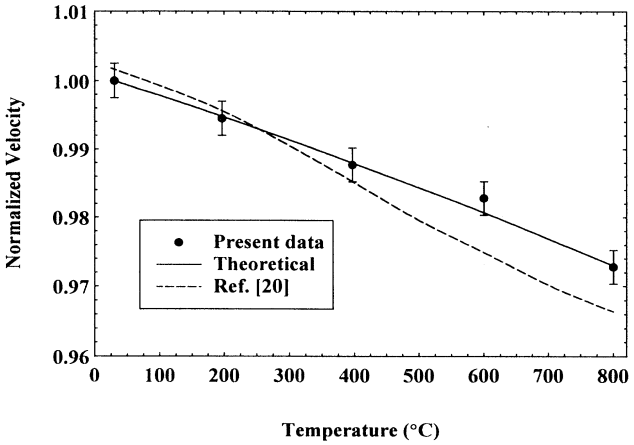

FIG. 4. Normalized SAW velocity along [100] in (001) n-type silicon. The dashed curve is a least squares fit to data from pulsed photoacoustic measurements (Ref. 20), while the solid curve is the result of calculations based on elastic constants (Ref. 12) and thermal expansion (Ref. 13) in this temperature range.

to their room temperature values.

The dashed line in Fig. 4 is reproduced from Schindel *et al.*,[20] where it serves as a least squares fit to SAW velocity data obtained from their pulsed photoacoustic method. This technique has not yet been extended to directions other than [100] and a rather large sample was required to prevent ambiguity arising through the untimely arrival of bulk waves or reflections. Although the authors claim an error in their measurements that can largely account for the difference between their results and the calculated curve in Fig. 4, the small scatter of their data suggests a more systematic source of error. Various other methods for measuring the angular dependence of SAW velocities have been applied to the (001) surface of silicon,[21] but to the best of our knowledge, none of these have been extended to high temperatures.

Slight systematic variations are apparent in Fig. 3, such as the 600 °C data which tend to lie above the theoretical curve (notwithstanding the 0.53% correction). These variations point to a slight difference between the temperature dependent elastic constants obtained ultrasonically for p-type silicon and used in the calculation, and the elastic constants that apply here in the Brillouin-scattering hypersound regime for n-type silicon. It would appear that the Brillouin scattering data are sufficiently accurate to reflect the expected small variations in elastic properties with impurity concentration. It would therefore be of great interest to derive the bulk properties from the angular dependence of SAW velocities. Although this inverse problem has received considerable attention recently,[16,18,22] the issue is beyond the scope of the present paper.

IV. CONCLUSION

These first high-temperature Brillouin-scattering measurements of SAW velocity angular dependence demonstrate the potential value of the technique for future studies of the elastic properties of opaque materials at high temperatures. The method described here holds particular promise for small samples, reactive materials, and thin films, which may be difficult (if not impossible) to deal with using conventional high-temperature techniques. There is good agreement between the measurements and theoretical predictions based upon thermal expansion and ultrasonic measurements of bulk elastic constants. This broad agreement, together with the finer detail apparent in the data, encourages the application of suitable inverse methods to extract bulk elastic constants of single crystals.

[1] O. L. Anderson, D. Isaak, and H. Oda, Rev. Geophys. **30**, 57 (1992).
[2] G. W. Meetham, J. Mater. Sci. **26**, 853 (1991).
[3] C. R. A. Catlow, Annu. Rev. Mater. Sci. **16**, 517 (1986).
[4] J. D. Comins, P. E. Ngoepe, and C. R. A. Catlow, J. Chem. Soc. Faraday Trans. **86**, 1183 (1990); E. S. Zouboulis and M. Grimsditch, J. Appl. Phys. **70**, 772 (1991); J. Xu and M. H. Manghnani, Phys. Rev. B **45**, 640 (1992).
[5] P. E. Ngoepe and J. D. Comins, Phys. Rev. Lett. **61**, 978 (1988).
[6] S. M. Lindsay, M. W. Anderson, and J. R. Sandercock, Rev. Sci. Instrum. **52**, 1478 (1981).
[7] R. Mock, B. Hillebrands, and J. R. Sandercock, J. Phys. Instrum. **20**, 656 (1987).
[8] F. Nizzoli and J. R. Sandercock, in *Dynamical Properties of Solids*, edited by G. K. Horton and A-A. Maradudin (North-Holland, Amsterdam, 1990), p. 281.
[9] J. G. Dil, Rep. Prog. Phys. **45**, 285 (1982); J. R. Sandercock, in *Light Scattering in Solids III*, edited by M. Cardona and G. Güntherodt, Topics in Applied Physics Vol. 51 (Springer, New York, 1982), p. 173.
[10] A. N. Stroh, J. Math. Phys. **41**, 77 (1962); V. R. Velasco and F. García-Moliner, J. Phys. C **13**, 2237 (1980).
[11] G. Farnell, in *Physical Acoustics*, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1970), p. 109.
[12] M. Ezz-el-Arab, B. Galperin, J. Brielles, and B. Vodar, Solid State Commun. **6**, 387 (1968).
[13] B. N. Dutta, Phys. Status Solidi **2**, 984 (1962).
[14] J. R. Sandercock, Solid State Commun. **26**, 547 (1978).
[15] R. Loudon and J. R. Sandercock, J. Phys. C **13**, 2609 (1980).
[16] M. W. Elmiger, J. Henz, H. v. Kanel, M. Ospelt, and P. Wachter, Surf. Interface Anal. **14**, 18 (1989); M. W. Elmiger, Doctoral thesis, ETH Zurich, 1988.
[17] A. E. Kadyshevich, V. M. Beilin, Yu. Kh. Vekilov, O. M. Krasil'nikov, and V. N. Podd'yakov, Fiz. Tverd. Tela Leningrad **9**, 1861 (1967) [Sov. Phys. Sol. State **9**, 1467 (1968)].
[18] M. Mendik, S. Satish, A. Kulik, G. Gremaud, and P. Wachter, J. Appl. Phys. **71**, 2830 (1992).

[19] A. G. Every and A. K. McCurdy, *Numerical Data and Functional Relationships in Science and Technology*, edited by D. F. Nelson, Landolt-Börnstein, New Series Group III, Vol. 29 (Springer, Berlin, 1992).

[20] D. W. Schindel, D. A. Hutchins, S. T. Smith, and B. Farahbakhsh, J. Acoust. Soc. Am. **95**, 2517 (1994).

[21] R. G. Pratt and T. C. Lim, Appl. Phys. Lett. **15**, 403 (1969); J. O. Kim and J. D. Achenbach, Thin Solid Films **214**, 25 (1992).

[22] V. G. Mozhaev, V. V. Aleksandrov, and A. K. Khmelev, in *Ultrasonics International '91* (Butterworth-Heinemann, Oxford, 1991).