Solid State Communications, Vol.39, pp.625-629.
Pergamon Press Ltd. 1981. Printed in Great Britain.

0038-1098/81/290625-05$02.00/0

# THE ONE PHONON RAMAN SPECTRUM IN MICROCRYSTALLINE SILICON

H. Richter, Z.P. Wang+, and L. Ley

Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1,
7000 Stuttgart 80, Federal Republic of Germany

Received May 15, 1981, by Manuel Cardona

The red shift and the broadening of the Raman signal from microcrystalline silicon films is described in terms of a relaxation in the q-vector selection rule for the excitation of the Raman active optical phonons. The relationship between width and shift calculated from the known dispersion relation in c-Si is in good agreement with available data. An increase in the decay rate of the optical phonons predicted on the basis of the same model is confirmed experimentally.

The first order Raman spectrum provides a fast and convenient method to determine whether a silicon film is crystalline or amorphous. The conservation of phonon momentum $\vec{q}$ in crystalline silicon leaves as Raman active mode only the zone center (q=0) optical phonon at $\omega$ = 522 $cm^{-1}$, which gives rise to a single line with a natural linewidth of ∿3.5 $cm^{-1}$ at room temperature. In amorphous silicon (a-Si) the $\vec{q}$-selection rule does not apply due to the loss in long range order. All phonons are therefore optically allowed and the Raman spectrum resembles the phonon density-of-states with a broad prominent hump at 480 $cm^{-1}$. Thus the observation of this hump or the sharp line at 522 $cm^{-1}$ differentiates between amorphous and crystalline Si.

In some instances spectra intermediate between the two extreme cases described above have been reported. They always involve a shift of the 522 $cm^{-1}$ line towards lower energy that is accompanied by a broadening. Morhange et al.[3] observed red shifts up to 7 $cm^{-1}$ (to 515 $cm^{-1}$) on laser annealed Si wafers that had previously been amorphized by ion bombardment. The maximum width was 8 $cm^{-1}$ (full width at half maximum, FWHM). Tsu et al.[4] report Raman lines that cover the range from 512 $cm^{-1}$ to 476 $cm^{-1}$ on thin silicon films that were obtained by the plasma decomposition of $SiF_4$ and $H_2$. Again the linewidth increases with decreasing energy.

Both groups surmised that the observed shifts had to do with an incomplete or incipient crystallization of the silicon films This conjecture was substantiated by the work of Iqbal et al.[5] who showed that poly crystalline films with a measured grain size of the order of 100 Å showed Raman spectra similar to the ones observed by Morhange et al. and Tsu et al. It was further established that the red shift of the 522 $cm^{-1}$ line increases with decreasing crystallite size.

In this communication we present a model that accounts for the observed shift and broadening in microcrystalline silicon ($\mu$c-Si). We give furthermore experimental evidence for an increase in the decay rate of the optical phonons of $\mu$c-Si that is predicted by the model. The main ingredient of the model is a relaxation of the conservation of crystal momentum in the creation and the decay of phonons in microcrystals. The wave function of a phonon with wave vector $\vec{q}_o$ in an infinite crystal is

$$\phi(\vec{q}_o,\vec{r}) = u(\vec{q}_o, \vec{r})e^{-i\vec{q}_o\cdot\vec{r}} \quad (1)$$

where $u(\vec{q}_o, \vec{r})$ has the periodicity of the lattice. In a crystallite assumed to be spherical with a diameter L the phonon is restricted to the volume of the crystallite. We impose this localization in the simplest possible manner in that we replace $\phi$ by a new function $\psi$ according

$$\psi(\vec{q}_o,\vec{r}) = A\exp\{-\frac{r^2}{2}/(\frac{L}{2})^2\}\phi(\vec{q}_o,\vec{r}) \quad (2)$$
$$= \psi'(\vec{q}_o,\vec{r}).u(\vec{q}_o,\vec{r})$$

with

$$|\psi|^2 = A^2\exp\{-r^2/(\frac{L}{2})^2\} \quad (3)$$

+Permanent address:
Institute of Semiconductors,
Academia Sinica, Beijing, China

That is, $\psi$ is localized to $|r| \lesssim L$ in the form of a gauss-distribution of width $\sqrt{\ln 2}$ L. $\psi'$ might be expanded in a Fourier series:

$$\psi'(\vec{q}_o,\vec{r}) = \int d^3q C(\vec{q}_o,\vec{q}) e^{i\vec{q}\cdot\vec{r}} \quad (4)$$

where the Fourier coefficients $C(\vec{q}_o,\vec{q})$ are given by

$$C(\vec{q}_o,\vec{q}) = \frac{1}{(2\pi)^3} \int d^3r \, \psi'(\vec{q}_o,\vec{r}) \, e^{-i\vec{q}\vec{r}} \quad (5)$$

Inserting $\psi'$ from eq. (2) into this expression yields

$$C(\vec{q}_o,\vec{q}) = \frac{AL}{(2\pi)^{3/2}} \exp\{-\tfrac{1}{2}(\tfrac{L}{2})^2(\vec{q}-\vec{q}_o)^2\} \quad (6)$$

Thus the $\psi'$ and therefore the $\psi$ are no longer Eigenfunctions of the phonon wave vector $\vec{q}_o$ but rather a superposition of Eigenfunctions with $\vec{q}$ vectors in an interval $|q-q_o| \lesssim 1/2L$ centered at $\vec{q}_o$. For our particular choice of localization (eq. (3)) the Eigenfunctions are weighted through the coefficients $C(\vec{q}_o,\vec{q})$ according to a Gaussian distribution. This implies that the phonon transition matrix elements $|\langle\vec{q}_o|\hat{O}|\vec{q}\rangle|^2$ have nonvanishing values also for $\vec{q}\neq\vec{q}_o$ according to:

$$|\langle\vec{q}_o|\hat{O}|\vec{q}\rangle|^2 = |\langle\vec{q}_o|\hat{O}|\vec{q}_o\rangle|^2 . C(\vec{q},\vec{q}_o)^2 , \quad (7)$$

where $\hat{O}$ is the photon-phonon interaction operator. In writing eq. (7) we have made the simplyfying assumption $u(\vec{q},\vec{r}) = u(\vec{q}_o,\vec{r})$. The localization of the phonon is in effect a relaxation of the $\Delta q = 0$ selection rule.

Here we are dealing in particular with the excitation of the zone-center ($\vec{q}$=o) optical phonon in silicon. Allowing transitions with $\vec{q}\neq$o will add contributions to the Raman spectrum at energies $\omega$ that are determined by the dispersion relations $\omega(\vec{q})$. Away from $\vec{q}$=o the degeneracy of the optical phonons is lifted into the transverse and the longitudinal optical phonons and the dispersion of both branches is negative.[6] It is obvious then that the additional transitions with $\vec{q}\neq$o will lead to a broadening of the Raman line by an amount $\Gamma_1$ and a concomitant red shift $\Delta\omega$ of its mean position. $\Delta\omega$ and $\Gamma_1$ are related to each other through the dispersion relation $\omega(\vec{q})$ and the coefficients $C(\vec{q},\vec{o})$ in eq. (6).

Figure 1 gives the relationship between $\Delta\omega$ and the linewidth $\Gamma$ calculated for a range of $\Delta q$ values in silicon. $\Gamma$ is the geometrical sum of the intrinsic width $\Gamma_o$ of the zone-center phonon and the additional width $\Gamma_1$ due to the phonon dispersion. The shape of the curve in Fig. 1 is independent of the details of the phonon dispersion as long as we assume it to be parabolic near $\Gamma$, the region we are dealing with here. On the right side ordinate of Fig. 1 we have indicated the magnitude of the parameter L used to derive the quantities $C(\vec{q}_o,q)$ in

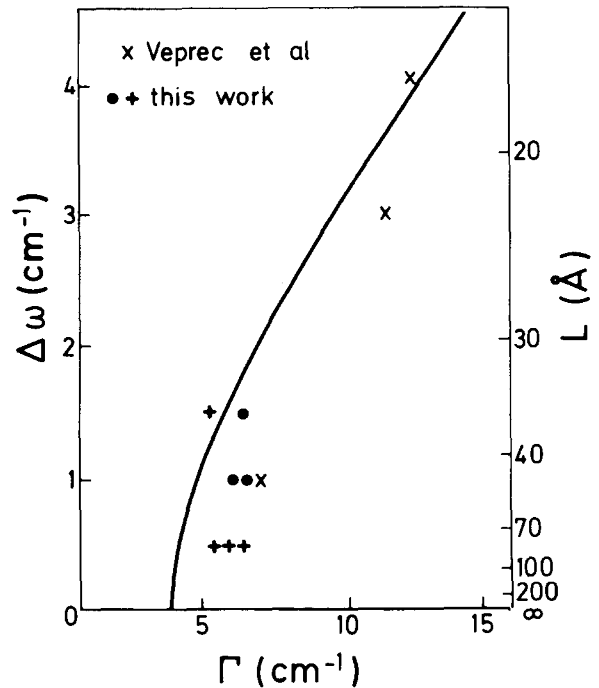


Fig. 1. Relationship between shift and width $\Gamma$ of the Raman line in microcrystalline silicon. The points are from measurements on microcrystalline Si films prepared by the plasma transport method. Crosses are values taken from Ref. 5. $\Gamma$ is corrected for spectrometer resolution.

eq. (6). The L's are related to the size of the crystallites via eq. (3). The numerical values are appropriate for the LO branch of the phonon dispersion in the direction $\Gamma$-X. They should not be taken literally, however, because they are model dependent.

Also shown in Fig. 1 are some experimental points of films that were prepared by the plasma transport method and data extracted from the spectra shown in the paper of Iqbal et al.[5] The $\Gamma$ values are corrected for the instrumental resolution. It appears that the experimental points follow the calculated relationship as well as can be expected taking the uncertainty of $\sim \pm 0.5$ cm$^{-1}$ in $\Gamma$ and $\Delta\omega$ into account. The crystallite sizes calculated are low by about 20 Å in all cases compared to the estimates by Iqbal et al.[5] and our own measurements in agreement with the nature of L as model parameter.

The shifts observed by Tsu et al.[4] exceed the limits of Fig. 1. The smallest shift in their work is 10 cm$^{-1}$ and the corresponding width is 32 cm$^{-1}$. Extending our calculation to $\Delta\omega$ = 10 cm$^{-1}$ we obtain $\Gamma$ = 31.5 cm$^{-1}$. It should be noted that some of the samples in Ref. 4 were heavily doped. An upward shift in the Raman line due to the electron-phonon interaction is

expected in these cases that opposes the down shift due to the finite crystallite size.

The Raman lines for microcrystalline samples are asymmetric with some tailing towards lower Raman shifts. This asymmetric lineshape is also well reproduced by our model as shown in Fig. 2. The calculation has been performed for L = 40 Å and the resulting line is shifted by 0.3 $cm^{-1}$ in Fig. 2 to align it with the measured spectrum. The extra intensity below 515 $cm^{-1}$ in the measured spectrum is due to contributions from amorphous regions in the sample.

The decay of the zone-center optical phonon in c-Si is again subject to the wave vector conservation rule. According to Klemens[8] the dominant decay channel is therefore the creation of two acoustical phonons of equal and opposite wave vector so that they add up to zero. We can write the corresponding transition probability $\Gamma_o(\omega_o)$:

$$\Gamma_o(\omega_o) \;\alpha\; |M|^2 \cdot N(\omega') \cdot N(\omega'')$$
$$\omega' = \omega'' = \tfrac{1}{2}\omega_o = 261 \text{ cm}^{-1} \qquad (8)$$

where M is the transition matrix element and $N(\omega)$ is the density of acoustical phonon states at the energy $\omega$.

If we relax the wave vector conservation in a microcrystal eq. (8) is replaced by:

$$\Gamma_o(\omega_o) \;\alpha\; |M|^2 \int F(\vec{q}_-, \vec{q}_+) N(\omega_o/2 - \omega') \cdot N(\omega_o/2 + \omega') \, d\omega' \qquad (9)$$

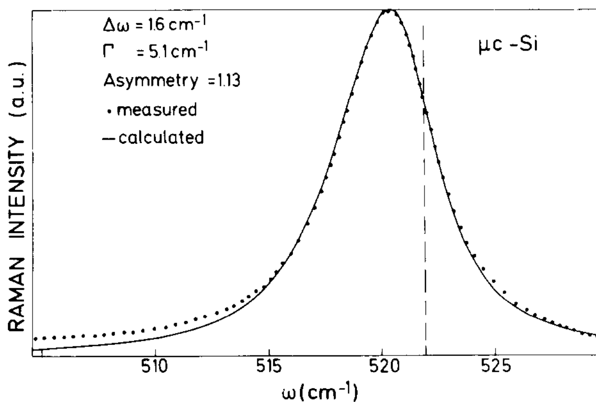


Fig. 2. Measured and calculated Raman line of a μc-Si sample. The dashed line indicates the Raman shift for c-Si. The asymmetry is defined as a/b, where a and b are the halfwidths of the Raman line.

The integration is limited to a range of energies $\omega'$ through the weighing function $F(q_-, q_+) = F(|\vec{q}(\omega_o/2 - \omega') - \vec{q}(\omega_o/2 + \omega')|)$. We assume that $F(q_-, q_+)$ is a Gaussian of width $\Delta q$, centered around $\vec{q}(\omega_o/2)$.

We expect an increase in $\Gamma_o$ whenever the averaged two phonon density of states defined through eq. (9) exceeds the two phonon density of states at $\omega_o/2 = 261$ $cm^{-1}$. $\Gamma_o$ enters the temperature dependence of the Raman linewidth $\Gamma$ according to[9]

$$\Gamma^2(T) = \Gamma_o^2 \left(1 + \frac{2}{e^x - 1}\right)^2 + \Gamma_1^2 \qquad (10)$$

where $x = h\omega_o/2kT$. $\Gamma_1$ is the temperature independent contribution to the linewidth of microcrystals discussed above. The geometrical addition of the two components is only an approximation since neither $\Gamma_o$ nor $\Gamma_1$ are Gaussians. The widths of Raman spectra measured as a function of temperature for a single crystal of silicon and 3 microcrystalline samples prepared at different temperatures $T_D$ are displayed in Fig. 3. The lines are fits to the data points using eq. (10) and the parameters $\Gamma_o$ and $\Gamma_1$ are listed in Table I. The values of $\Gamma_o$ and $\Gamma_1$ are only weakly correlated in the fits. $\Gamma_1$ is determined by $\Gamma(T)$ for $T \to 0$ and $\Gamma_o$ is mainly determined through the slope of $\Gamma(T)$ for large T. We find that $\Gamma_o$ increases with increasing values of $\Gamma_1$, i.e. with decreasing crystallite size. This is in accord with the phonon dispersion of Si. In the last column of Table I we give the values $L = 1/\Delta q$ calculated from eq. (10) with the aid of the phonon dispersion and phonon density of states for c-Si.[6] The values of L between 80 and 100 Å are in good agreement with transmission electron micrographs of these samples. In particular the increase in crystallite size with higher deposition temperatures has been established earlier. The value of $\Gamma_o$ for c-Si is slightly smaller than the 2.1 $cm^{-1}$ measured by Hart et al.[9] possibly due to improved measurement techniques.

In summary, we have presented a model that accounts for the observed variations in the position and shape of Raman spectra of microcrystalline silicon. The model is a simple extension of the Raman effect in crystalline Si, taking into account the relaxation of the phonon wave vector due to the small crystallite size. We do not claim that other effects such as surface phonons or deviations from the diamond structure in μc-Si can be excluded at the present time. The quantitative agreement between our calculations and the measurements

TABLE I. Parameters obtained from a fit to the temperature dependent Raman linewidths in 4 silicon samples.

| sample | $\Gamma_1(cm^{-1})$ | $\Gamma_o(cm^{-1})$ | $\frac{\Gamma_o}{\Gamma_o(cryst)}$ | L(Å) |
|---|---|---|---|---|
| cryst. Si | 0 | 1.7 | 1 | ∞ |
| μc-Si, $T_D$=300°C | 1.8 | 2.0 | 1.18 | 100 |
| μc-Si, $T_D$=250°C | 2.7 | 2.1 | 1.24 | 90 |
| μc-Si, $T_D$=175°C | 4.4 | 2.5 | 1.47 | 80 |

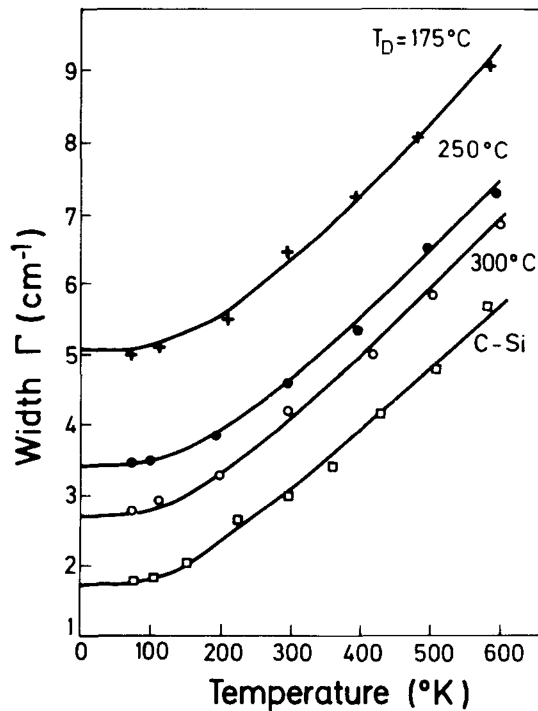


Fig. 3. Raman line width Γ vs. temperature for crystalline Si and 3 μc-Si samples. The solid lines are the result of a fit explained in the text. Γ has been corrected for the spectrometer resolution.

indicates, however, that the relaxation of the wave vector selection rule plays a significant role in μc-Si.

ACKNOWLEDGEMENT

We are indebted to M. Cardona for a number of illuminating discussions.

## REFERENCES


1. PARKER. Jr., J.H., D.W. FELDMAN, and M. ASHKIN, Phys. Rev. 155, 712 (1967)
2. SMITH, J.E., M.H. BRODSKY, B.L. CROWDER, M.I. NATHAN, and A. PINCZUK, Phys. Rev. Lett. 26, 642 (1971)
3. MORHANGE, J.F., G. KANELLIS, and M. BALKANSKI, Solid State Commun. 31, 805 (1979)
4. TSU, R., M. IZU, S.R. OVSHINSKY, F.H. POLLAK, Solid State Commun. 36, 817 (1980)
5. IQBAL, Z., A.P. WEBB, and S. VEPREK, Appl. Phys. Lett. 36, 136 (1980)
6. WEBER, W., Phys. Rev. B 15, 4789 (1977)
7. RICHTER, H., L. LEY (to be published)
8. KLEMENS, P.G., Phys. Rev. 148, 845 (1966)
9. HART, T.R., R.L. AGGARWAL, and B. LAX, Phys. Rev. B 1, 638 (1970)
10. KANELLIS, G., J.F. MORHANGE, and M. BALKANSKI, Phys. Rev. B 21, 1543 (1980)
11. KOBLISKA, R.J., S.A. Solin, Phys. Rev. B 8, 3799 (1973)