

Isotopic Mass and Lattice Constants of Si and Ge: X-ray Standing Wave Measurements

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Abstract The molecular volume of materials depends on their isotopic mass. This effect is purely quantum-mechanically in origin, since it arises from the combined effect of the zero-point motion of the atoms and the anharmonicity of the potential. Associated differences are thus small. We measured the isotopic mass dependence of the lattice constants of Si and Ge with high accuracy. Scaled to a mass difference of $\Delta M = 1 \text{ amu}$ we find values of $(\Delta a/a)$ of -0.36×10^{-5} and -0.88×10^{-5} for Ge at 300K and 30K, respectively. For Si, scaled to $\Delta M = 1$, we find -1.8×10^{-5} and -3.0×10^{-5} at 300K and 30K, respectively. Our results represent a stringent test for theoretical calculations. The agreement is good with published results for Ge but less good with the two existing calculations for Si.

1 Introduction

The influence of the isotopic composition on the properties of materials is attracting increasing interest lately [1]. The reason for this is twofold. On the one hand, one obvious reason is the increased availability of isotopic pure elements and substances since after the end of the cold war isotope separators can now be used for peaceful purposes. On the other hand, materials with tailored isotopic composition are attracting growing interest because of their - sometimes exotic - features. Primarily influenced by the specific isotopic composition are the vibrational properties. Diamond made of isotopic pure ^{13}C , for example, should thus be harder than natural diamond and was suggested to be the hardest substance known to man [2]. The thermal conductivity of isotopic pure crystals can considerably exceed the values for the corresponding natural substances [3]. Thus, isotopically pure materials may have interesting applications where extreme stress tolerance and heat dissipation is required and isotopically pure crystals have, e.g., successfully been used as x-ray monochromators for third generation synchrotron sources [4]. Likewise are the electronic properties affected by the isotopic composition, although these influences are less dramatic. Compared to the result of the isotopic mass on the vibrational properties of crystals, the effect on the structure via changes in the molecular volume are subtle. For heavier elements only of the order of $\Delta d/d = 10^{-6}$ is expected at room

temperature for a 1% change of mass. However, even such subtle differences must be taken into account in some cases. E.g., present attempts to improve the accuracy in the determination of Avogadro's number in order to replace the archival Pt/Ir kilogram, kept at Sèvres near Paris, by an atomic standard are resting upon the precise determination of the silicon lattice constant and this in turn is eventually influenced by the isotopic composition [5].

The dependence of the lattice constant of crystals on their isotopic mass is purely a quantum-mechanical effect. It originates from the zero-point motion of the atoms in association with the anharmonicity of the potential which is also responsible for the temperature dependence of the molar volume. Following the early work of London [6], a few theoretical papers have been published recently on the issue of lattice constant versus isotopic mass [7–9]. Since the associated changes are very small, there are hardly any experimental data available. Measurements are additionally hampered by the fact that the lattice constant difference is largest at 0K and almost vanishes at temperatures above the Debye temperature of the particular crystal. Thus, until recently, the effect had been determined reliably only for diamond because (a) diamond has a very high Debye temperature and thus the lattice constant difference is almost at its maximum even at room temperature, (b) the relative mass difference is high, and (c) highly perfect crystals of diamond can be produced, allowing fairly accurate lattice constant measurements with standard diffraction techniques. However, diffraction techniques are bound to fail to provide precise lattice constant values for crystals with smaller relative mass differences and with low Debye temperatures. Thus, the results of an earlier study for the lattice constant difference between natural germanium and an enriched ^{74}Ge crystal using a modified diffraction technique [10] were later found to be in considerable disagreement with theoretical calculations [7].

We demonstrated lately [11] that the x-ray standing wave technique [12,13] can be used to determine lattice constant differences with very high accuracy. For a thorough description of the principle of the method we

refer the reader to our recently published work [11] and restrict ourselves here to a brief outline. By Bragg diffraction, an interference field is generated in a substrate of a certain isotopic composition on which an homoepitaxial film with a different isotopic composition is grown. The planes of the interference field are accurately in registry with the lattice planes of the substrate and thus, this is essence of the method, serve as a yardstick for the position of the *surface planes* of the overlayer. These are displaced by N times the lattice mismatch from the position which they would adopt if the epilayer would have had the same isotope composition as the substrate. Here, N is the number of lattice planes of the overlayer. Furthermore, the mismatch of the lattice planes normal to the surface is increased for a pseudomorphic, epitaxial layer compared to the lattice mismatch for an unstrained system by a factor ϵ since the film is in registry at the interface. Thus, the difference in lattice constant normal to the surface is enhanced as determined by the Poisson ratio.

By scanning a suitable Bragg reflection of the substrate crystal in angle or in energy, as in the present case, the planes, i.e. maxima and minima, of the x-ray standing wave move inward, antiparallel to the \mathbf{Q} -vector by half the spacing of the diffracting planes [13]. The position of the surface planes of the isotopically modified epilayer in reference to the extrapolated bulk planes is assessed by recording the emitted photoelectrons while scanning the chosen Bragg reflection of the substrate with the diffraction vector (\mathbf{Q} -vector) normal to the growth surface.

2 Experimental

Epitaxial films were grown on Ge(111) and Si(111) by molecular beam epitaxy (MBE) [11] and liquid phase epitaxy (LPE), respectively. Isotopically enriched ^{76}Ge films (86 % ^{76}Ge , 14 % ^{74}Ge), with a thickness of $1.36 \pm 0.09 \mu\text{m}$ and $0.56 \pm 0.01 \mu\text{m}$, were grown on the (111) surfaces of a natural and an isotopically highly enriched (96% ^{70}Ge , 4% ^{72}Ge) single crystal [14], respectively. The isotopically enriched Si film (60 % ^{30}Si , 40 % ^{28}Si) with a thickness of $0.92 \mu\text{m}$ was grown by liquid phase epitaxy on a perfect single crystal Si(111) substrate with natural isotopic composition (91% ^{28}Si , 4% ^{29}Si , 5% ^{30}Si). Thickness and isotopic composition of the films had been determined with Rutherford backscattering spectrometry (RBS) and secondary ion mass spectroscopy, respectively [15]. The x-ray standing wave measurements [16] were carried out using $\text{Cu-K}\alpha$ radiation from a stationary x-ray tube and at the Hamburg Synchrotron Radiation Laboratory (HASYLAB), using synchrotron radiation from the DORIS storage ring which was monochromatized by a Si(333)/Si(511) crystal combination with a bandpass of 0.3 eV at the energies at which the measurements were performed (around 7.59 keV for Ge and 8.00 keV for Si). The samples were mounted strain free on the cold finger of a He flow-

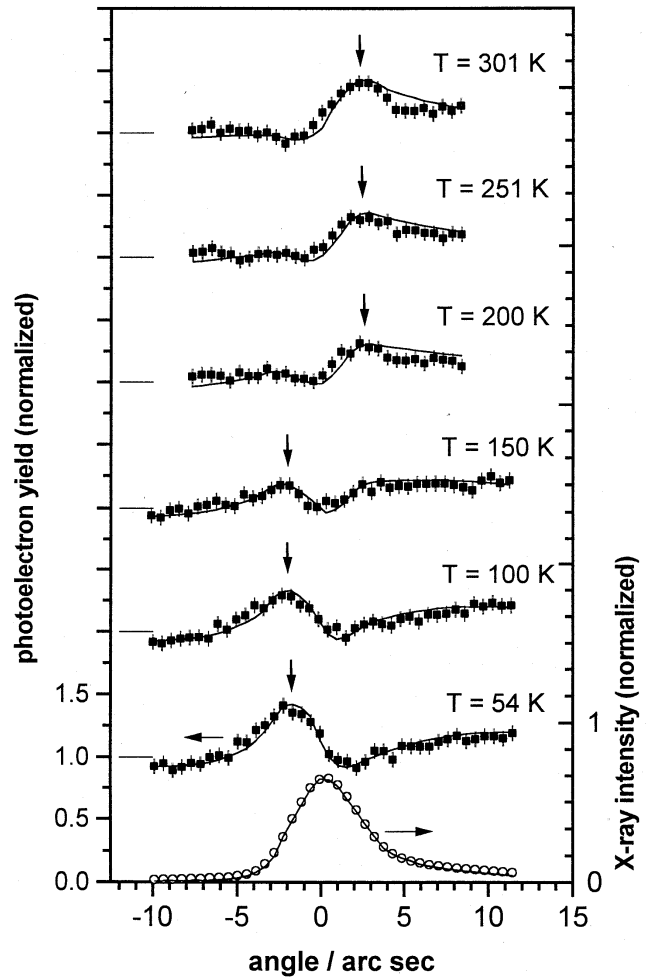


Fig. 1 Ge(333) reflectivity and photoelectron yield from a $1.36 \mu\text{m}$ epitaxial ^{76}Ge layer on $^{nat}\text{Ge}(111)$ as a function of glancing angle θ for different temperatures (from ref. [11]). The solid lines are fits to the experimental data (symbols). The fit to the reflectivity determines the angular scale and fits to the photoelectron signal yield the surface phase shifts from which the d-spacing is calculated.

through cryostat with a diode temperature sensor placed close by. The total yield of the emitted photoelectrons was detected with a channeltron [17]. For the standing wave measurements, the monochromator was scanned in energy, passing the Bragg reflections of Si and Ge. For Si we chose the (333) reflection, whereas for Ge we chose the (444) reflection at a Bragg angle close to 90° . The $^{70}\text{Ge}(111)$ substrate crystal showed a mosaic spread of 0.3° . However, this did not compromise the accuracy of our measurement since the acceptance of the crystal is $> 0.3^\circ$ close to normal incidence.

3 Results and Discussion

The results of several XSW scans as a function of temperature are shown for ^{76}Ge on natural Ge(111) in Fig.

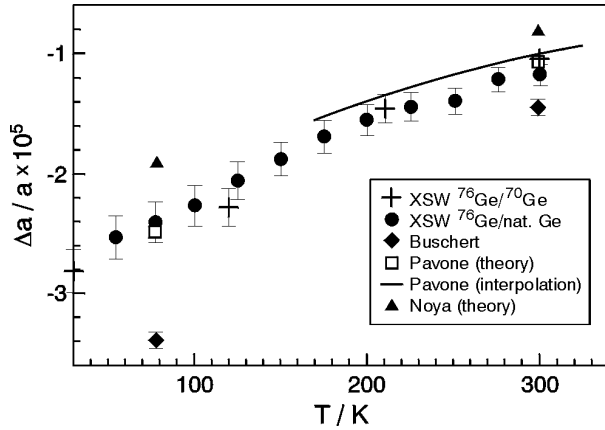


Fig. 2 The lattice constant difference of Ge with isotopic mass as a function of temperature. All data are scaled to a mass difference of $\Delta M = 3.05$ amu. Shown are the results of our recently published work [11] (solid dots) and the present XSW measurements (crosses) in comparison with existing calculations [7,9] and the results of earlier diffraction measurements by Bushert et al [10].

1. The change in the shape of the photoelectron yield curves with changing temperature can clearly be distinguished and is a signature for the change in the lattice constant difference between the substrate and the epilayer. Shown are also fits to the experimental data from which the value of the lattice constant difference for the surface layer of the thin film are deduced. To calculate the change in lattice constant, the elastic constants of Ge must be considered and the measured lattice mismatch has to be divided by a factor of 1.37 [19]. The experimental results obtained for the dependence of the lattice constant difference on the Ge isotope mass as a function of temperature are shown in Fig. 2. Data and calculations are scaled to $\Delta M = 3.05$. The outcomes of both sets of XSW measurements agree very well with each other and support the calculations of Pavone and Baroni [7].

The corresponding results for silicon, also corrected with the help of the elastic constants [19] (a correction factor of 1.44 for Si), are shown in table 1. For comparison, we are also listing values calculated by Herrero [20] and Biernacki and Scheffler [21]. We deduced them from the plots shown in those publications and compile them here for convenience. All lattice constant differences are scaled to $\Delta M = 1.06$ for silicon. The calculations of Herrero agree within the limits of error with our data whereas the calculations of Biernacki and Scheffler differ by about 30%. However, it is worth noting that the error of the calculations published by Herrero is about twice as large as our experimental error, too large to show the anomaly in the lattice expansion of Si below 150K which is clearly reflected in our experimental data and qualitatively shown in Biernacki and Schefflers calculation.

Table 1 Lattice constant difference for Si isotopes of different mass scaled to $\Delta M = 1.06$

T (K)	XSW results $\Delta a/a$ $\times 10^{-5}$	Herrero [20] $\Delta a/a$ $\times 10^{-5}$	Biernacki&Scheffler [21] $\Delta a/a$ $\times 10^{-5}$
0	-	-2.7	-4.1
30	-3.2	-	-4.2
90	-3.1	-	-4.2
100	-	-2.2	-
150	-2.9	-2.5	-3.9
180	-2.6	-	-3.5
200	-	-2.3	-
210	-2.5	-	-3.3
240	-2.3	-	-3.0
300	-2.0	-1.9	-2.5
	$\pm 6\%$	$\pm \approx 12\%$	

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- The crystal had been produced by the Bridgman technique.
- In the homoepitaxial Si layer, RBS had shown thickness fluctuations of 10 %.
- The experimental set up is described in reference [11].
- In this way the recorded electron signal was originating from a certain depth which was taken into account in the analysis [11,18].
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