Polarizabilities of Isolated Silicon Clusters

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Z. Naturforsch. **50a**, 445–452 (1995); received November 14, 1994

Dedicated to Prof. Dr. E. Wicke on the occasion of his 80th birthday

The static electric polarizabilities α of silicon clusters with up to 60 atoms have been measured employing a mass selective molecular beam deflection method. The polarizability per atom $\alpha_N = \alpha/N$ of the Si_N-clusters has been investigated for Si_{11} and the size ranges $N = 14-28$, $22-34$, $28-44$, $34-50$, $41-58$, and $42-68$. The results show that the polarizability per atom decreases from $N = 11$ until a minimum at $N \approx 28$ is reached. The polarizability per atom increases for $N \geq 28$, passes through a maximum at $N \approx 36$ and finally converges between $N \approx 50-70$ against the value $\alpha_N = 1.9$ Å^3. If the model of a homogeneous dielectric sphere is applied to the larger clusters one calculates that the value $\alpha_N = 1.9$ Å^3 corresponds to a dielectric constant of $\varepsilon = 3.2$. This value is significantly smaller than the dielectric constant of bulk silicon $\varepsilon_b = 11.8$.

The present paper focuses on the maximum in the polarizability at $N \approx 36$. This effect is discussed with special emphasis to recent Car-Parinello calculations which have predicted cage-like silicon structures that enclose a core of several highly coordinated atoms. This structure suggests an improved dielectric sphere model where the core is represented by a smaller sphere with its own dielectric constant ε_c. It is shown within this model that the observed maximum in polarizability is due to a significant enhancement of the core dielectric constant to a value of $\varepsilon_c \approx 50$. This enhancement is related by means of a simple model to the effect that silicon becomes metallic under high pressure.

1. Introduction

The properties of silicon are of major scientific and technological interest, and considerable research effort has expended on it [1]. Over the last decade, particular attention has been focussed on the electronic properties of silicon nanostructures such as quantum dots, quantum wires and quantum wells [2]. Much of the activity is motivated by the large number of potential applications of these mesoscopic systems. Due to their dimensions these systems are characterized by huge surface to volume ratios. The crucial role played by the surface in the electronic properties is due to the fact that the typical length scale of the electronic wave functions [3], characterized by the exciton ground state radius [4]

$$r_{\text{exciton}} = \frac{\varepsilon \varepsilon_0 h^2}{\pi m_r^{\text{eff}} e^2} \tag{1}$$

of the electron-hole pairs, can reach the dimensions of these systems. This radius is usually estimated by employing the reduced effective mass and the static dielectric constant of bulk crystalline silicon. This is because not much is known about the evolution of the bulk silicon dielectric properties as a function of particle size.

However, it is well known that there are significant differences between most physical and chemical properties of finite clusters and bulk matter. Thus, the present study was undertaken in order to obtain a clearer understanding of the size evolutionary patterns of the dielectric properties of silicon clusters. Specifically, we report herein the first determination of the polarizabilities of neutral silicon clusters containing 11–68 atoms. Polarizability measurements are especially well suited to resolve the question raised above, since polarizabilities of clusters [5] and molecules [6] are very sensitive to their electronic and geometric structure.

While much progress has been made in the past to learn about the electronic properties of negatively and positively charged Si_N-clusters [7–9], there is relatively little unambiguous size-specific information on the corresponding properties of the neutral clusters [10], but the following experimental observations are known: The ionization energy exhibits a rapid decrease for clusters containing more than 21 atoms [11, 12]. Indications of a strong size dependence of the

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Reprint requests to Prof. F. Hensel.

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electronic structure in the cluster size range with 24–34 atoms have been found in the optical absorption spectra of size-selected matrix-isolated neutral Si_N-clusters [13].

The chemical reactivity of several silicon cluster ions [14] exhibits deep minima in silicon clusters containing 33, 39 and 45 atoms. Special features, which are consistent with the existence of two structural isomers, are also found in the behaviour of the drift mobility of size-selected silicon cluster cations in rare gases in the size range with 24–34 atoms per clusters [15].

There have been several attempts to study the properties of neutral silicon clusters theoretically. Ab-initio [16] and local density functional [17] calculations have been performed to study the structures and energies of small Si_N-clusters with 2–14 atoms. The lowest energy calculated structures correspond to the cage-like arrangements, e.g. a pentagonal bipyramid for Si_7 and octahedral or prismatic geometrical arrangements for Si_8-Si_{10}.

Cage-like structures have also been calculated for larger clusters with 20–45 atoms employing the Car-Parrinello method [18]. Unexpectly, these calculations reveal a novel structural pattern for midsized silicon clusters with more than 25 atoms. These structures are formed by two shells of atoms, the outer one (cage) being fullerenelike and the inner one (core) consisting of a few atoms saturating dangling bonds. The coordination between the encaged atoms, which are linked with each other, is strongly increased. It is noteworthy that the calculated gaps between the highest occupied and the lowest unoccupied molecular orbitals of these clusters are all of the order of a few tenths of an electron volt. These values are remarkably smaller than the corresponding gaps from 0.5 to 2.5 eV of small clusters with 2–14 atoms [17] and the 1.2 eV band gap of bulk silicon [19].

Accordingly, the polarizability measurements of the present work are particularly suited to provide experimental evidence for these theoretically predicted unforeseen structural patterns of silicon clusters [18], since polarizabilities are very sensitive to changes in the electronic gap energies and indeed we find significant agreement with the predictions of [18].

2. Apparatus and Experimental Method

The static dipole polarizability of isolated particles can be measured by deflecting a highly collimated molecular beam of these particles in an inhomogeneous electric field. Deflections occuring are proportional to the dipole moment times the electric field gradient. Results obtained are then interpreted in terms of induced moments, the mean static polarizability α being averaged over the relevant molecular states. Then, as the induced dipole moment and the field gradient are both proportional to the electric field E, one calculates for the deflections

$$d = C \frac{\alpha E^2}{m v^2}, \tag{2}$$

where α is the polarizability, m the particle mass, v its velocity and C the apparatus function which includes the geometry of the inhomogeneous electric field and the flight path length from the deflecting field to the detector. A detailed description of this method and its application to atoms and molecules is given by Miller and Bederson [20]. The adaptation of this method for the study of metal clusters by combining the deflection profiles with time of flight mass spectrometry (TOF-MS) profiles has recently been reviewed by de Heer [5, 21].

A schematic overview of the apparatus used in the present investigations is shown in Figure 1. The silicon cluster beam is produced by a pulsed laser-vaporization source. Since the details of its construction have been described in [22] we give only a brief description here. A silicon rod is irradiated with the focussed light from the evaporation laser. A small amount of silicon vapour is formed and then cooled in a flow of helium gas where it condenses to form clusters. The helium-silicon cluster mixture is expanded out through a temperature controlled nozzle into a vacuum chamber, thereby producing a supersonic beam of silicon clusters.

The inhomogeneous electric field used in the present experiment for deflection is the electric analogue of the so called "two-wire-magnetic-field" first developed by Rabi et al. [23]. The advantage of this field is that the product of the electric field E_z and its gradient $\partial E_z/\partial z$, i.e. $E_z \cdot \partial E_z/\partial z$, is constant over the dimensions of the molecular beam. The experimental setup of the deflection plates is similar to the one used by Bederson et al. [24].

The scanning unit and the TOF-MS is shown in Figure 2. The deflection profiles are measured by means of collimated excimer laser light. The collimated light beam is reflected by two adjustable mirrors that can be shifted by two stepping motors. In the

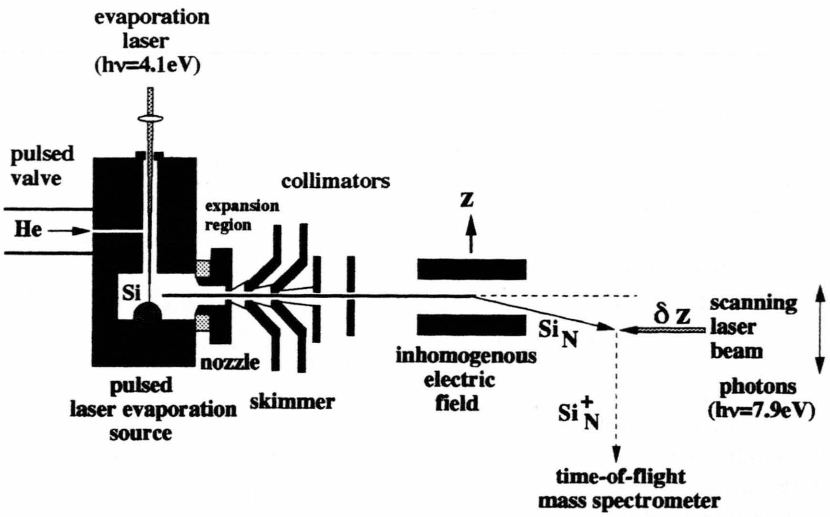

Fig. 1. Schematic overview of the cluster beam apparatus.

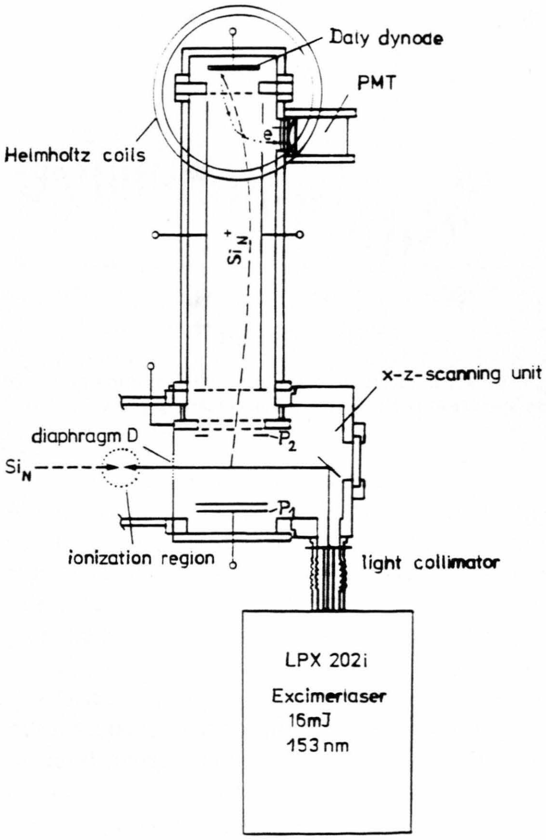

Fig. 2. Scanning unit and time-of-flight mass spectrometer (TOF-MS).

present experiment the x-position is fixed and the z-position is shifted. Typical beam profiles are shown in Figure 4. The scanning position can be measured with an accuracy of ±0.005 mm. The ionization of the particles takes place in a distance of 15 cm from the TOF-MS as shown in Figure 2. The mass spectrometer is a three stage time-of-flight mass spectrometer with a large ion volume ($4 \times 4 \times 4$ cm^3) [25, 26].

The ionization of the clusters in front of the TOF-MS gives the possibility to remove cations out of the TOF-MS that are generated by photofragmentation and photoionization of residual gases. These cations are generated due to the high photon energy $h\nu = 7.89$ eV that has to be used in order to overcome the high ionization potentials [11] of silicon clusters. They can seriously adulterate the mass spectra of the clusters and hamper accurate measurements with low intensity semiconductor cluster beams.

In the present experiment this problem has been overcome by developing a new kind of TOF-MS mode [27]. The principle of this mode is based on the fact that the clusters and residual gas molecules differ significantly in their velocity components. While the ionized clusters fly with a well defined velocity into the TOF-MS, the ionic products of the residual gas molecules have an isotropic thermal velocity distribution in all directions. Therefore all the clusters, even if they are slightly deflected by the deflection plates ($d < 1$ mm), enter the mass spectrometer through the small diaphragm D whereas only a minute amount of residual gas molecules statistically enters the spectrometer. Typically 300 μs after the photoionization when the cluster cations have reached the zone between the acceleration plates P1 and P2 of the TOF-MS, these plates are switched on and the cluster cations are detected. However, there are still photocations coming from residual gas that have been also ionized directly between the acceleration plates P1 and P2. They still heavily contaminate the cluster mass spectrum (see Figure 3 b). In order to get rid of this contamination we switch +400 V for about 100 μs on the acceleration plate P2 directly after photoionization. The silicon clusters are still outside the TOF-MS and not effected by this cleaning pulse because the electric stray fields are confined to the region between P1 and P2 shielded by a grounded net placed behind the entrance diaphragm *D*. The residual gas cations are removed and clean silicon cluster spectra can be obtained if the acceleration plate P2 is switched on for a second time when the cluster cations have entered the acceleration plates zone.

The advantage of employing the TOF-MS mode described before is demonstrated in Figure 3. In the mass spectrum performed without the cleaning pulse only the larger clusters with $N > 17$ can be properly analyzed and all the smaller clusters disappear in the background. However, in the mass spectrum performing with the cleaning pulse all the clusters with lower ionization potentials than $h\nu = 7.89$ eV are visible with no contamination of organic cations.

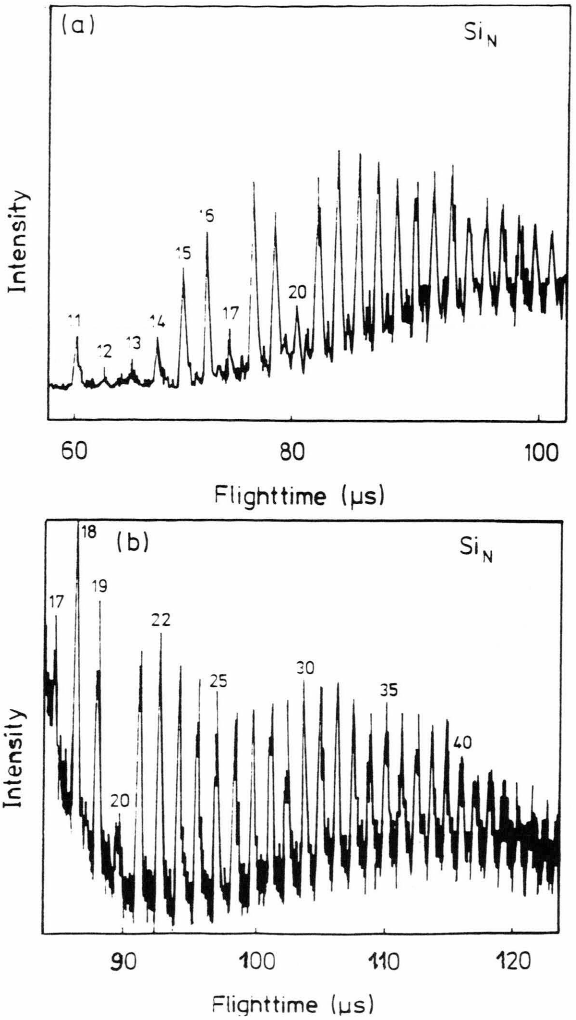

Fig. 3. (a) Mass spectrum performed with cleaning pulse. (b) Mass spectrum performed without cleaning pulse.

3. Results and Discussion

3.1. Polarizabilities of Silicon Clusters

The polarizabilities of Si_{11} and several cluster size ranges have been measured by the above described deflection technique. Up to now size ranges could be investigated because of the very low counting rates due to the highly collimated silicon cluster beam. The polarizabilities are determined by measuring cluster beam deflection profiles in dependence of the deflection plate voltage *U* which is directly proportional to the electric field *E* in (2). Figure 4 shows two typically profiles for silicon clusters in the size range $N = 42-48$ for $U = 0$ and $U = 33$ kV. The profiles are significantly shifted, while their shape remains unchanged. The shape remains unchanged for all cluster size ranges that have been investigated in this work. We found no shoulders or any other evidence for different polarizabilities for the two structural isomers of silicon cluster cations postulated by Jarrold [15] in the size range $N = 24-34$. However this can be due to the restricted resolution of the present experimental setup. A higher collimation of the beam ($\ll 0.5$ mm) leads to too low cluster intensities.

If the deflections *d* are plotted against the electrode voltages *U* one expects according to (2) a straight line through the origin with a slope that is proportional to the average polarizability α. Such a plot is shown in Fig. 5 for two silicon and aluminum cluster ranges ($N = 28-44$ and $N = 42-68$). The aluminum cluster deflections have been recorded for calibration since

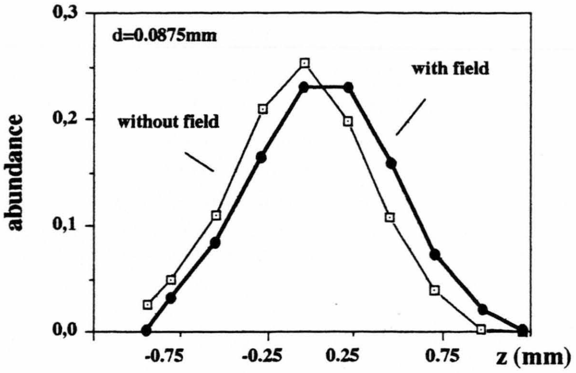

Fig. 4. Beam profiles: Raw data.

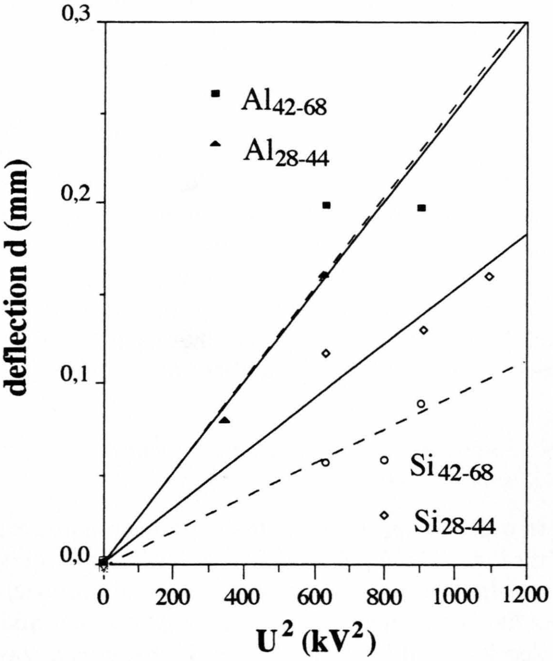

Fig. 5. Silicon cluster beam deflections d against electrode voltages U.

their polarizabilities are well known from the experiments of de Heer et al. [21]. The comparison between the slopes for silicon and aluminum clusters allows an accurate determination of the silicon cluster polarizabilities. Moreover, the additional investigation of the aluminum cluster deflections gives also a direct comparison of the dielectric behaviour of a metal and a semiconductor which are neighbours in the periodic table.

The size dependence of the polarizabilities per atom α_N of the silicon clusters is shown in Figure 6 (in units of $4\pi\varepsilon_0$). First, we focus on the largest cluster sizes with $N = 50-60$ atoms. The polarizability of the silicon clusters is significantly smaller than the polarizability of the aluminum clusters. At the first glance this is expected especially for larger clusters since the bulk dielectric constant of the metallic bulk aluminum is $\varepsilon_b(\mathrm{Al}) = -\infty$ whereas the value for the semiconducting bulk silicon is only $\varepsilon_b(\mathrm{Si}) = 11.8$ [28]. However the value for the silicon clusters is much lower than expected from its bulk dielectric constant. This can be demonstrated by modelizing the clusters as a dielectric sphere with dielectric constant ε.

Its polarizability is then given by

$$\alpha_N = 4\pi\varepsilon_0 \frac{(\varepsilon - 1)}{(\varepsilon + 2)} R_{\mathrm{WS}}^3, \tag{3}$$

where

$$R_{\mathrm{WS}} = \left(\frac{3\,V_{\mathrm{m}}}{4\pi N_{\mathrm{A}}}\right)^{1/3} \tag{4}$$

denotes the Wigner-Seitz-radius that can be calculated by means of the molar volume V_{m} and the Avogadro constant N_{A}. The Wigner-Seitz-radius for the silicon bulk diamond structure is $R_{\mathrm{WS}} = 1.68$ Å. By use of this value and the bulk dielectric constant $\varepsilon_b = 11.8$ one obtains for the polarizability per atom $\alpha_{N,\mathrm{diamond}} = 3.72$ Å^3. This value is included in Fig. 6 and demonstrates that the measured polarizabilities of the larger silicon clusters with $N \approx 60$ are much smaller than the polarizabilities expected from macroscopic silicon. If the calculation is reversed one finds that the measured polarizability $\alpha_N = 1.9$ Å^3 for the

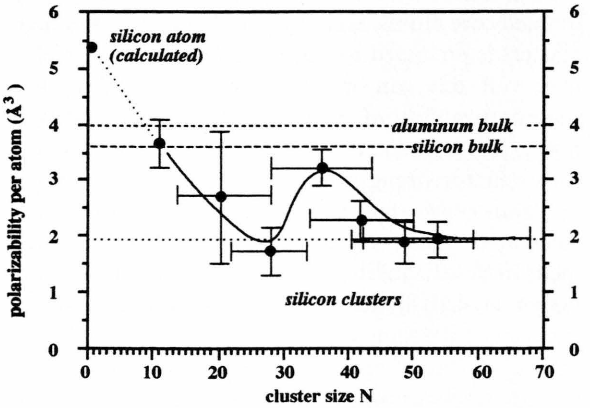

Fig. 6. Size dependence of silicon cluster polarizabilities.

larger silicon clusters corresponds to a dielectric constant of $\varepsilon = 3.2$. One can hence alternatively state that the polarizabilities of the larger clusters correspond to a dielectric constant which is much smaller than the bulk dielectric constant.

In the dielectric sphere model one can explain the low polarizability either by a small dielectric constant or by a Wigner-Seitz-radius that is significantly smaller than for the bulk diamond structure. The present experiments can furthermore not decide if both effects are present. However recent drift mobility measurements on silicon cluster cations by Jarrold et al. [15] indicate that a more compact structure and hence a smaller Wigner-Seitz-radius has to be assumed in order to understand the mobility of the cations. The results are interpreted in terms of a β-tin structure [15] with a Wigner-Seitz-radius of $R_{\mathrm{WS}} = 1.58$ Å. Even if we also use this Wigner-Seitz radis for the neutral silicon clusters one has still to insert a very low value of $\varepsilon = 3.8$ for the dielectric constant.

3.2. *Size Dependence of Silicon Cluster Polarizabilities*

Figure 6 shows that the polarizability per atom increases from the value of $\alpha_N = 1.9$ Å^3 at $N \approx 60$ with decreasing cluster size, reaches a local maximum of $\alpha_N = 3.2$ Å^3 at $N \approx 40$ and drops again very close to the original value of $\alpha_N = 1.9$ Å^3 at $N \approx 28$. This enhancement of polarizability occurs just in the size range where Röthlisberger et al. [18] have predicted the cage like structures containing several highly coordinated core atoms. Since the band gap of these silicon clusters is predicted to be only a few tenth of an electron volt one can speculate by means of (6) that the polarizability of such a cluster can be relatively high. However, since we know nearly nothing about the oscillator strengths it is better to find a more phenomenological approach to the question how these calculated structures can be related to an enhancement in polarizability. It has been noted by Röthlisberger et al. [18] that the high coordination of the encapsulated atoms in the cage is similar to the enhanced coordination in silicon under high pressure. It is furthermore known that silicon under high pressure ($p > 120$ kbar) [29] is metallic, and hence one can expect that the core region of the highly coordinated atoms is quasimetallic and highly polarizable.

In order to quantify this idea we suggest an improved dielectric sphere model that consists of an inner sphere with high dielectric constant ε_{C} which represents the highly coordinated atoms, and an outer shell with low dielectric constant ε_{S} for the surface atoms. The polarizability of this model can be calculated by classical electrostatics [30] and is given by

$$\alpha_\alpha = 4\pi\varepsilon_0 \left(\frac{3(\varepsilon_{\mathrm{C}} - \varepsilon_{\mathrm{S}}) - (u/t)^3(\varepsilon_{\mathrm{C}} + 2\varepsilon_{\mathrm{S}})}{(u/t)^3(\varepsilon_{\mathrm{C}} + 2\varepsilon_{\mathrm{S}})(\varepsilon_{\mathrm{S}} + 2) - 2(\varepsilon_{\mathrm{C}} - \varepsilon_{\mathrm{S}})(1 - \varepsilon_{\mathrm{S}}} + 1 \right) u^3, \tag{5}$$

where u and t are the radii of the outer and inner sphere. We assume for the dielectric constant of the shell the value $\varepsilon_{\mathrm{S}} = 3.2$ that has been found for the larger clusters with $N \approx 60$. The measured polarizability per atom $\alpha_N = 3.2$ Å^3 for a silicon cluster with $N \approx 36$ corresponds then according to (5) with $u \approx 2t$ to a dielectric constant $\varepsilon_{\mathrm{C}} = 50$ for the core. The cluster core in this model is hence nearly metallic. The decrease of the polarizability for smaller and larger cluster sizes than $N \approx 36$ is in this model due to a smaller dielectric constant of the cluster core and hence it indicates a smaller coordination of the atoms in these clusters. This result is consistent with the work of Röthlisberger et al. [18] that mentions a decrease of the coordination number from Si_{36} to Si_{45}.

3.3. *Polarizability and Electronic Structure of Silicon Clusters*

In order to approach the theoretical consequences of the low value of polarizability for the larger clusters it is helpful to use a quantum mechanical approach that has been applied in a similar way to atoms and molecules by Miller et al. [20]. Neglecting dipolarization effects the polarizability per atom of an isotropic quantum mechanical system can be related to its electronic structure by means of the formula

$$\alpha_N = \frac{e^2 h^2}{4\pi^2 m_e N} \sum_J \frac{F^z_{J0}}{(E_J - E_0)^2}\,. \tag{6}$$

where E_J are the energy eigenvalues of the system and F^z_{J0} are the oscillator strength of the optical transitions $|0\rangle \rightarrow |J\rangle$. The sum over all oscillator strengths F^z_{J0} is according to the sum rule of Thomas, Reiche and Kuhn [31] identical with the number of valence electrons in the cluster. In the case of silicon each atom contributes with 4 electrons to the total number of valence electrons:

$$\sum_J F_{J0}^z = 4N. \tag{7}$$

If (7) is inserted in (6) one can express the polarizability per atom in terms of the probabilities

$$w_{J0} = \frac{F_{J0}^z}{\sum_J F_{J0}^z} \tag{8}$$

as

$$\alpha_N = \frac{e^2 h^2}{\pi^2 m_e} \sum_J \frac{w_{J0}}{(E_J - E_0)^2}. \tag{9}$$

In order to get an idea of which are the optical transitions $|0\rangle \rightarrow |J\rangle$ and the corresponding energy differences $E_J - E_0$ that predominantly contribute to the sum in (9) we define an effective "optical energy gap" E_{eff} by

$$\frac{1}{E_{\text{eff}}^2} = \sum_J \frac{w_{J0}}{(E_J - E_0)^2}. \tag{10}$$

This effective optical energy gap is then directly related to the polarizability per atom α_N by

$$E_{\text{eff}} = \frac{e h}{\pi (m_e \alpha_N)^{1/2}}. \tag{11}$$

The measured polarizabilities $\alpha_N = 1.9$ Å^3 for the larger clusters correspond to an effective optical energy gap of $E_{\text{eff}} = 15.2$ eV. However, it has to be pointed out that the polarizability which is calculated from the bulk dielectric constant also corresponds to a quite large effective band gap of $E_{\text{eff}} = 10.9$ eV. A similar trend to high band gap values is also found by means of the solid state models. For the ideal silicon bulk one calculates by means of the Penn model [32] a value of $E_{\text{eff}}^{\text{Penn}} = 4.8$ eV. This energy is identical with the ionization potential of bulk silicon [11] and is obviously much larger than the smallest difference $E_{\text{min}} = 1.2$ eV between the highest occupied and the lowest unoccupied band. This deviation is related to selection rules. The oscillator strength that correspond to the transitions into states near the conduction band edge has to vanish and transitions towards higher energies dominate the polarizability. This is not at all surprising, especially because silicon is an indirect semiconductor.

However the effective optical energy gap of 15.2 eV for the clusters is much higher than obtained from the Penn model for the bulk. The value which results from the polarizability (11) can only be explained by an important contribution of electronic states above the ionization threshold of the cluster to the polarizability. But this is not surprising, because it is well known that about 50% of the oscillator strength of the hydrogen atom results from such states above the ionization threshold [31]. However the origin of the low silicon cluster polarizabilities for respectively the contributions from transitions into highly excited states is not understood up to now. The perturbation theory demonstrates nevertheless that the small polarizability of the silicon clusters is related to strong contributions from states with $E \approx 15$ eV. In terms of one electron excitations these are states highly above the ionization threshold. Other possible contributions are for example collective electronic excitations like plasmons [33]. In any case one expects a significant blue shift in the optical spectra of the silicon clusters with $N \approx 60$ compared to the silicon bulk spectra.

Conclusion

The static electric polarizabilities of isolated silicon clusters have been investigated in a molecular beam experiment. It turns out that the measured polarizability values of the largest clusters with $N \approx 60$ atoms are significantly lower than expected from the bulk dielectric constant. A consequence of this low value is a significant blue shift of the optical transitions in these clusters compared to bulk silicon. Enhanced polarizabilities have been observed in the size range with $N = 30-50$ where cage like cluster structures containing several highly coordinated core atoms have been theoretically predicted. This enhancement in polarizability has been related to the effect that silicon under high pressure becomes metallic due to an increased coordination.

Acknowledgement

We want to thank Dr. W. Stolz (Wissenschaftliches Zentrum für Materialwissenschaften und Fachbereich Physik, Philipps-Universität Marburg) for his advices concerning the semiconductor materials.

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