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Ultraviolet photoelectron spectroscopy of Si_4^- to Si_{1000}^-

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Abstract. Using a new experimental setup we have measured UV ($h\nu = 6.4$ eV) photoelectron spectra of cold silicon cluster anions Si_n^- in a very broad size range. For sizes up to $n = 46$ the spectra exhibit rich structures. For larger sizes only smooth spectra have been obtained. No trace of a bandgap has been found even for clusters with more than 1000 atoms.

PACS. 36.40.Mr Spectroscopy and geometrical structure of clusters – 33.60.Cv Ultraviolet and vacuum ultraviolet photoelectron spectra – 71.24.+q Electronic structure of clusters and nanoparticles

1 Introduction

Silicon clusters and nanoparticles have attracted very strong interest during recent years. One of the reasons for this interest is their possible application in optoelectronics [1]. A wealth of experimental and theoretical work has been performed ([2–5] and references therein). For the determination of the cluster structures mobility measurements [5] and anion photoelectron spectroscopy [4] turned out to be especially useful. Up to now high quality photoelectron spectra were only available for Si_4^- to Si_{20}^-. Here we present a new set of photoelectron data which extends this region up to Si_{1000}^-.

2 Experiment

The apparatus used in this experiment will be described in detail in a forthcoming publication, and is only briefly sketched here. The clusters are produced by a gas aggregation source [6]. Inside a liquid nitrogen cooled aggregation tube a magnetron sputter source injects silicon vapour into a mixture of helium and argon, which leads to cluster formation. Due to the magnetron discharge a large portion of these clusters is charged. The charge state depends on the cluster electron affinity. In the case of silicon the anion intensity is even higher than that of the cations. By changing source parameters like sputtering power, gas pressure, gas composition and aggregation length the mean cluster size produced can be tuned from a few atoms up to a few ten thousand atoms. After expansion into the vacuum the clusters are inserted into a high resolution double-reflectron time-of-flight mass spectrometer, where a multiwire mass gate positioned at the focus point of the first reflector can be used to select single cluster sizes with a selectivity of up to $m/dm = 2000$. The size selected clusters are then decelerated and inserted into a magnetic bottle photoelectron spectrometer, where they are irradiated by an ArF excimer laser ($h\nu = 6.4$ eV). The spectrometer has been optimized for the use of UV light. At the laser intensity used (about 1–3 mJ/cm^2) the typical total background photoelectron intensity is only a few percent of the cluster photoelectron intensity, so background subtraction is not necessary. In most cases the photoelectron spectra have been averaged over 10000 laser shots.

3 Results

Fig. 1 shows the series of photoelectron spectra obtained. The results for the smallest clusters ($n = 4$ to 20) are in very good agreement with UV-spectra published earlier [4,7,8], although some details are better resolved here, which is probably due to the low cluster temperature. Furthermore the spectra of these small clusters are in excellent agreement with simulations [2,4]. The clusters with sizes $n = 20$ to $n = 44$ exhibit rich structures as well, which have not been observed up to now. There is a nice correspondence between these results and the ion mobility measurements by Hudgins *et al.* [5]. They have shown that between $n = 27$ and $n = 30$ the cluster structure changes from prolate to more-spherical. This transition is also visible in the photoelectron spectra. From $n = 20$ to $n = 26$ (with the exception of $n = 23$ and $n = 25$) all spectra exhibit very similar profiles. Between $n = 27$ and $n = 30$ the spectra then suddenly become rather featureless, which hints at the presence of two or more isomers in the beam, which is in accordance with the observations of Hudgins *et al.* At $n = 31$ then a new profile emerges,

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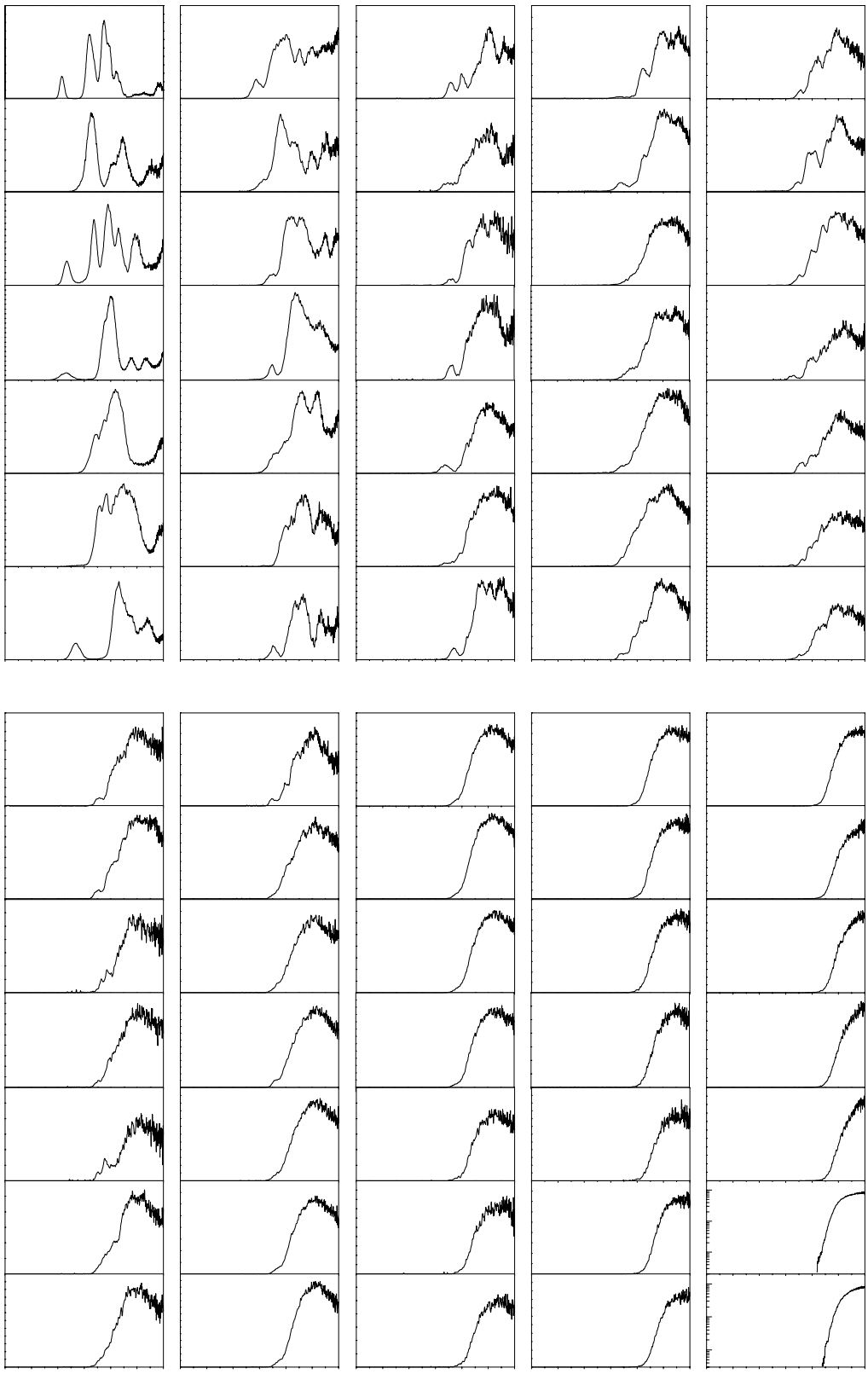

Fig. 1. Photoelectron spectra of silicon cluster anions (6.4 eV photon energy). The spectra of Si^-_{500} and Si^-_{1000} are plotted on a logarithmic scale.

which is fully developed at $n = 33$. Some remainder of this structure can be observed up to $n = 40$. From $n = 41$ again a new pattern emerges, which persists up to $n = 44$. In this size range the mobility measurements of Hudgins *et al.* also seem to show some structural change, although not as clear as the one around $n = 29$. For larger sizes all of the spectra are rather smooth and featureless. This might be due to a high density of states, but is certainly also the result of the presence of several isomers. The larger clusters with up to $n = 1000$ show an only gradual onset at the detachment threshold. For the clusters up to $n = 100$ a shoulder is visible at the threshold which can be interpreted as the LUMO (lowest unoccupied molecular orbital) of the neutral cluster, which is occupied by the one additional electron. For the larger clusters this shoulder merges into the general slope of the occupied states. No trace of a band gap have been found even for $n = 1000$. If there was a band gap, that is a large HOMO-LUMO gap of the neutral cluster, one would expect to observe a peak separated from the main onset. As such a peak is expected to be small, we have plotted the spectra of Si_{500}^- and Si_{1000}^- on a logarithmic scale. Clearly no peak is visible. This was expected of course, as such clusters should have many surface states very close to the cluster "valence" band which will take up the one additional electron. It will be interesting to repeat this measurements with hydrogen passivated clusters, where this surface states should be saturated. Such experiments are underway.

4 Summary

We have measured anion photoelectron spectra for many cluster sizes between Si_4^- and Si_{1000}^-. For clusters with 21 to 44 atoms well structured spectra have been obtained, which should constitute a good test for calculations of the cluster properties. For larger sizes up to $n = 1000$ no trace of a bandgap has been found, which demonstrates the importance of surface states for the electronic structure of silicon clusters.

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