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SEMICONDUCTOR CLUSTER SURFACE CHEMISTRY

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ONR Cluster Science Workshop
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The combination of laser-vaporization supersonic cluster beam techniques with the technology of fourier transform ion cyclotron resonance, FT-ICR, has opened up a new approach to the detailed fundamental understanding of semiconductor surface chemistry. With this apparatus it is possible to trap clusters of a specific size in a superconducting magnet under ultrahigh vacuum conditions. Through collisions with an inert thermalizing gas it is possible to slowly cool the clusters down to room temperature, allowing them to anneal to the most stable possible form. In the case of silicon this technique has revealed that certain cluster sizes (eg. 21, 25, 33, 39, 45) are particularly stable and unreactive with reagents such as ammonia and ethylene. These clusters are believed to have taken highly symmetric crystalline forms with the bonding patterns on the surface resembling those found on bulk single crystals. Such special clusters should serve well as microscopic testing grounds for detailed theoretical predictions of semiconductor surface chemistry.

INTRODUCTION

In modern technology there is no industry more deeply concerned with the fundamental, atomic-level details of surfaces and interfaces than microelectronics. Silicon in particular is one of the most studied of all modern materials. Commercial, highly polished discs of single crystal silicon are among the purest materials known. The chemistry of their manufacture and subsequent processing into highly integrated microchips is highly evolved. Yet, even with silicon, we are in a state of great ignorance when it comes to making a detailed prediction of the chemistry or physics of even a single well-known site of a particular reconstructed surface of the perfect bulk crystal. Although STM has now finally revealed the actual structure of the (7x7) reconstruction of the (111) surface of silicon, the chemistry of the various sites on this surface is only beginning to be learned at the empirical level. Theory is still not in a position to reliably predict the reconstruction of an arbitrary surface of silicon, let alone the chemical consequences of that reconstruction. These statements apply to the surfaces of all the technologically important semiconductors and metals. By and large there is no predictive, fundamental surface chemistry for any semiconducting or metallic material.

The reason for this lack of detailed fundamental understanding of surfaces is partly due to the large number of atoms involved and the fact that they do not come from the first few rows of the periodic table. But the problem is deeper than that. Even if one picks off a small aggregate of surface atoms and considers just the nature of this small cluster, it rapidly becomes clear that this is a far more complicated object than what is normally dealt with in traditional chemistry or molecular physics. Chemistry generally deals with the properties of molecules which have a large gap between the ground electronic state and the first excited electronic state. When the molecule is in the ground electronic state, this gap makes the Born-Oppenheimer approximation valid, allowing one to talk about a molecular structure, and vibrational motions about this structure as distinct from the electronic degrees of freedom. The molecular orbitals then split cleanly into tightly bound core and occupied valence levels on one hand, and much weaker unoccupied virtual orbitals on the other. Most of modern chemistry is based on consideration of the "frontier orbitals" -- primarily the highest occupied molecular orbital (the HOMO) and the lowest unoccupied orbital (the LUMO). It is the ebb and flow of electrons in and out of these frontier orbitals that chemists usually use to guide their thoughts in predicting the reactive behavior of the vast number of known (and imagined) molecules.

What makes surfaces (and the small clusters derived from them) so difficult to understand is absence of a large HOMO-LUMO gap and the consequent breakdown of the separation of electronic and nuclear parts of the quantum mechanical problem. For example, consider just a 4 atom cluster of nickel atoms. Based on spectral probes of transition metal clusters over the past 10 years[1], it is now clear that Ni_4 has on the order of 10^4 excited electronic states with in the 1st eV above the ground electronic state (arising from the various ways of arranging the $3d^9$ holes on the four atoms). This tiny piece of nickel surface is already close to being metallic -- at least as far as its electronic "band" structure is concerned. Any chemical theory depending on HOMO-LUMO frontier orbital arguments is certainly very suspect in such a case. It is primarily for this reason that chemists are just about as befuddled as anyone else when asked to predict the reactive behavior of a real metallic surface. It's not so much that there are a lot of atoms, or that some of them are nickel. It's the large density of states near the Fermi energy.

Semiconductors should be easier than metals. At least they often have a substantial band gap. But this is true only for the bulk crystal lattice. On the surface the unreconstructed structure usually results in a metallic state, and the question of whether the restructuring of the annealed real surface ties up dangling bonds well enough to result in a gap in the surface density of states is quite subtle. When a reactant attacks a particular site on this surface, it is again quite unclear that frontier HOMO-LUMO orbital arguments so central to traditional chemical theory will ever have much predictive power. Yet these surfaces unquestionably have a rich and detailed chemistry, and the technological significance of understanding, modifying, and controlling this chemistry could be vast.

One common response to this question is that it is unrealistic to expect a detailed understanding of surface chemistry that is anywhere near as rich and predictive as -- say -- organic chemistry. But this subject of the chemistry of real surfaces may not always be as complex as it now seems. The history of physical science has many cases where forbiddingly complex phenomena were discovered to have simple, elegant, and precise explanations. In fact the chemistry of organic compounds provides an excellent example of this process of complexity reduction, extending over (roughly) just the past 100 years. Jumping ahead 100 years from now, it's hard for many of us to imagine that there won't be a good, fundamental, predictive science of surface chemistry in hand at least by then. If so, it is reasonable to ask (from the hypothetical viewpoint of the year 2090) how that science was developed.

Certainly, the study of actual bulk surfaces must have been involved, and the current approach of focussing attention on simple single crystal surfaces of well-defined cleavage planes and reconstructions is clearly a useful, albeit idealized, model. However, the purpose of this short paper is to emphasize that small clusters offer another type of idealized model of real surfaces. It is a model that has the advantage of an explicit molecular scale and should therefore be particularly useful in developing an understanding of the molecular-scale details of surface chemistry. Perhaps most important, it is a model where systematic small changes can be made (at least in principle) in the cluster size, charge, shape, temperature, surface chemisorption, ... , etc. in order to test the range of validity of any proposed theory. In a sense these small clusters provide a means for bringing surface chemistry to the theorist. The small, finite number of atoms and systematic modifiability make clusters an excellent testing ground for any new chemical theory of surfaces.

Compared with the bulk single crystal model, the technologies involved in working with these cluster models are still very much in their infancy. In the sections below one of the most promising new techniques for preparing and probing these little model surfaces is described with particular emphasis on silicon. Here there is now excellent evidence that special cluster "crystals" are formed for certain cluster sizes. It is on such microscopic (actually nanoscopic) cluster crystals that we hope to base this new approach to the fundamental study of surface chemistry.

FT-ICR of LEVITATED CLUSTERS

Figure 1 shows the schematic diagram of a supersonic cluster beam apparatus which produces cold cluster ions, directs them through the fringing field of a superconducting magnet, slows them down, and traps them in an fourier transform ion cyclotron resonance (FT-ICR) cell. The clusters are produced by a laser- vaporization supersonic beam source (not shown in the figure) developed nearly ten years ago at Rice[2]. Since its inception this source has proved to be a key enabling technology for the study of metal and semiconductor clusters. It permits fairly intense beams of clusters in the 2 to over 1000 atom size range to be produced routinely from virtually any element in the periodic table.

For the experiments described below this source was adapted to operate with a silicon wafer as the vaporization target, mounted in the supersonic nozzle so that the vaporization laser traced out a uniform spiral pattern as the wafer was rotated and translated. The source was adjusted to produce an intense cold beam of the singly-charged positive cluster ions which were accelerated to 700 eV and directed toward the superconducting magnet by the pulsed electric extraction and deflection electrodes shown in the upper right hand corner of Fig. 1. As these silicon cluster ions approach the high magnetic field one has to be careful that the so-called "magnetic mirror" effect does not slow the ions and ultimately bounce them back toward the source. As we demonstrated first several years ago[3], it is possible to avoid this problem by using a the einzel lens combination shown in Fig. 1 to insure that the cluster ions come in on converging trajectories such that they are tangent to the local magnetic field lines at the first point where they are significantly affected by the field. Under these conditions the ions effectively "hop on" to the local field lines and follow them smoothly into the bore of the magnet. The result is that it is now trivial to inject any cluster ion smoothly into the superconducting magnet without excessive excitation of the cyclotron motion. After the cluster ions have successfully passed through the fringing field of the magnet, it is straightforward to slow them down to a few eV by the pulsed electrostatic deceleration electrodes shown in Fig. 1. Clusters produced on successive shots of the pulsed supersonic source may be readily added together in the ICR trap by a sequence of pulse voltages on the initial "screen door" also shown in the Figure. The result of this technology is that virtually any cluster ion that can be produced in the pulsed supersonic beam can be injected in to the ICR trap and enough of these pulses can be added together so that the trap is filled[4-7].

Once in the ICR trap the clusters must be thermalized to the temperature of the trap (300K for the experiments discussed here). Due to the large magnetic field (60,000 gauss) and high vacuum quality of this apparatus, this thermalization process may be extended over a time period of 10-30 seconds in order to give the clusters plenty of time to gradually cool. Cooling occurs by both collisions with an inert buffer gas such as argon (over 10,000 collisions are normally possible without excessive cluster ion loss from the trap), and spontaneous infrared emission. This slow cooling has been found to be essential in order to allow the silicon clusters to anneal to their most stable crystalline form.

The mass spectrum of the contents of the trap can then be monitored at extremely high mass resolution by coherent excitation of the ion cyclotron motion, and detecting this motion by sensitively monitoring the image currents flowing to the side electrodes of the ICR trap. This time domain signal is digitized and the fourier transform is calculated. The resultant fourier transform ion cyclotron resonance (FT-ICR) spectrum then gives the mass spectrum with resolutions that easily exceed 10,000.

EVIDENCE FOR SPECIAL STRUCTURES WITH SILICON

Figure 2 shows a typical FT-ICR mass spectrum of silicon clusters in such an apparatus in the size range from 44 to 54 atoms[8]. Ordinarily one would expect to see a fairly broad distribution of masses for each silicon cluster as a result of the various isotopes of silicon in natural abundance. For the top panel of this figure, the clusters initially injected into the trap were cleaned up a bit by selective excitation of the cyclotron motion of cluster in the extremes of the isotopic mass distribution so as to leave a clean baseline between each cluster size.

As seen in this top panel of Fig. 2, there is no strong evidence that any cluster is significantly different than another. This is a general result for silicon cluster ions in this mass region: as they are made in the source there is no evidence for the "magic" number behavior that is often so striking with other elements (carbon, for example). However, the lower panel shows clearly that there is in fact something very different between some of the clusters such as Si_{45}^+, and the others. Here the FT-ICR mass spectrum is shown after the clusters prepared in the same way as that of the top panel were exposed to 4 seconds of collisions with NH_3 at 4×10^{-7} torr, which at the Langevin rate would correspond to 3000 collisions on the surface of a typical cluster. Note that the clusters with 44 and 46 atoms have nearly disappeared, being replaced by mass peaks corresponding to $Si_{44}NH_3^+$ and $Si_{46}NH_3^+$, for example. On the other hand, the mass peaks corresponding to Si_{45}^+ have remained virtually unchanged.

Results such as these led us several years ago to propose that special structures must be realized for silicon clusters with 21, 25, 33, 39, and 45 atoms[6]. Follow-up experiments performed in the intervening years in our laboratory have continued to verify this result: there is something very special about these clusters[8]. A number of theorists have been intrigued by this evidence[9-14] and have proposed a variety of possible unique structures to explain the observed special stability of such clusters as Si_{45}. One of the most appealing of these structural models is one proposed by Efthimios Kaxiras[9]. As shown in Fig. 3 it is a highly symmetric cluster where 5 atoms have the full tetrahedral bonding of the bulk diamond lattice, and the remaining 40 atoms are arranged in a pattern of 5- and 6-membered rings on the surface, each atom being 3-fold coordinated. As pointed out by Kaxiras, the "dangling bonds" on the cluster surface are arranged so as to form six pi-bonded chains running along the 6 edges of this over-all tetrahedral symmetry cluster. In other words, this cluster structure is very much like a piece of bulk silicon, with a surface restructuring much like the 2x1 reconstruction of Si(111).

In the past few months, however, conflicting results have been reported by the group of Martin Jarrold at AT&T Bell Labs[15]. Using a tandem quadrupole mass spectrometer device with a laser vaporization silicon cluster ion source much like our own, and a rather high pressure reaction drift cell between the two quadrupole mass spectrometers, the Bell Labs group was able to measure the reaction behavior of silicon clusters toward a variety of reactants. With ethylene as a reactant they obtained the surprizing result that little if any special behavior was observed for Si_{45} and the other clusters such as Si_{33}^+ and Si_{39}^+ which had been found to be specially unreactive in experiments in the FT-ICR apparatus at Rice. More importantly, they observed that there appeared to be many different forms of these large silicon clusters populated in their cluster ion beam, each with a different reaction rate toward ethylene chemisorption.

At the time the Bell Labs results were announced, the cluster FT-ICR apparatus at Rice was undergoing major revisions to permit direct down-axis injection of the supersonic cluster beam into the ICR cell. With this new machine we just recently have been able to go back and check the chemisorbtion behavior of Si_{45}^+ and its neighboring clusters with ethylene[16]. Figure 4 shows the first results of this experiment. In the top panel the mass spectrum is shown as it appears before ethylene is added. As with the experiment shown in Figure 2, this mass spectrum of the initial clusters has been cleaned up a bit by ejecting all but the most abundant 2 isotopic masses of each of the desired clusters. Since the mass of ethylene is roughly the same as a silicon atom, we have ejected all clusters except 39, 42, 45, 48, and 51 in order to be able to clearly detect the reaction products as they form. The small mass peaks seen 17 amu to higher mass of most of the silicon cluster peaks are due to a chemisorbed OH group arising from reaction with a small amount of H_2O contaminant in the ICR trap. The key result is seen in the lower panel of Figure 4 which shows the observed FT-ICR mass spectrum of the clusters after exposure to 1×10^{-5} torr of ethylene for 60 seconds. Note that $Si_{39}^+$and Si_{45}^+ display little if any reaction, whereas such clusters as Si_{42}^+ and Si_{51}^+ have been almost completely reacted away. So in sharp contrast to the Bell Labs experiment, silicon clusters in the ICR apparatus continue to show dramatic variations in reactivity as a function of cluster size with ethylene. In fact ethylene appears to be just as selective as ammonia in its chemisorption activity.

Obviously, there is something quite different in the silicon clusters being monitored in the tandem quadrupole beam experiment at Bell Labs and our ICR experiments at Rice. The current best hypothesis is that the single most critical difference is the vastly different time scale of the experiments. In the tandem quadrupole experiments, the clusters are probed within 1-2 milliseconds after their formation in the clusters source, whereas in the ICR apparatus the injection and thermalization process occurs over a 10-30 second time period, a difference in time scale of over four orders of magnitude. Our current belief is that for these larger silicon clusters this longer time scale is critical in order for the clusters to have time to anneal the most stable structure as they cool.

Proof that annealing is in fact possible has been provided very recently in an experiment where we have shown the effect of excitation with a XeCl excimer laser for silicon clusters in the ICR prior to reaction[17]. Figure 5 shows an example of the clear evidence for laser annealing that was found in these experiments. Laser annealing of large metal and semiconductor cluster ions levitated in a ICR trap is likely to become a major enabling technology over the next few years.

CONCLUSION

Under the length constraints of this short account it has been impossible to present anything approaching a full review of the many new techniques that have been developed recently for the preparation and study of metal and semiconductor clusters. ICR studies similar to those discussed above are particularly promising since they are beginning to show that it is possible to prepare well annealed clusters of a particular structure. Other examples have been found with clusters of carbon, gallium arsenide, and a variety of transition metals. These "cluster crystals" may well turn out to be exceedingly important in future efforts to obtain a fundamental, predictive understanding of surface chemistry.

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FIGURE CAPTIONS

Figure 1. Schematic of FT-ICR apparatus with supersonic cluster beam injection.

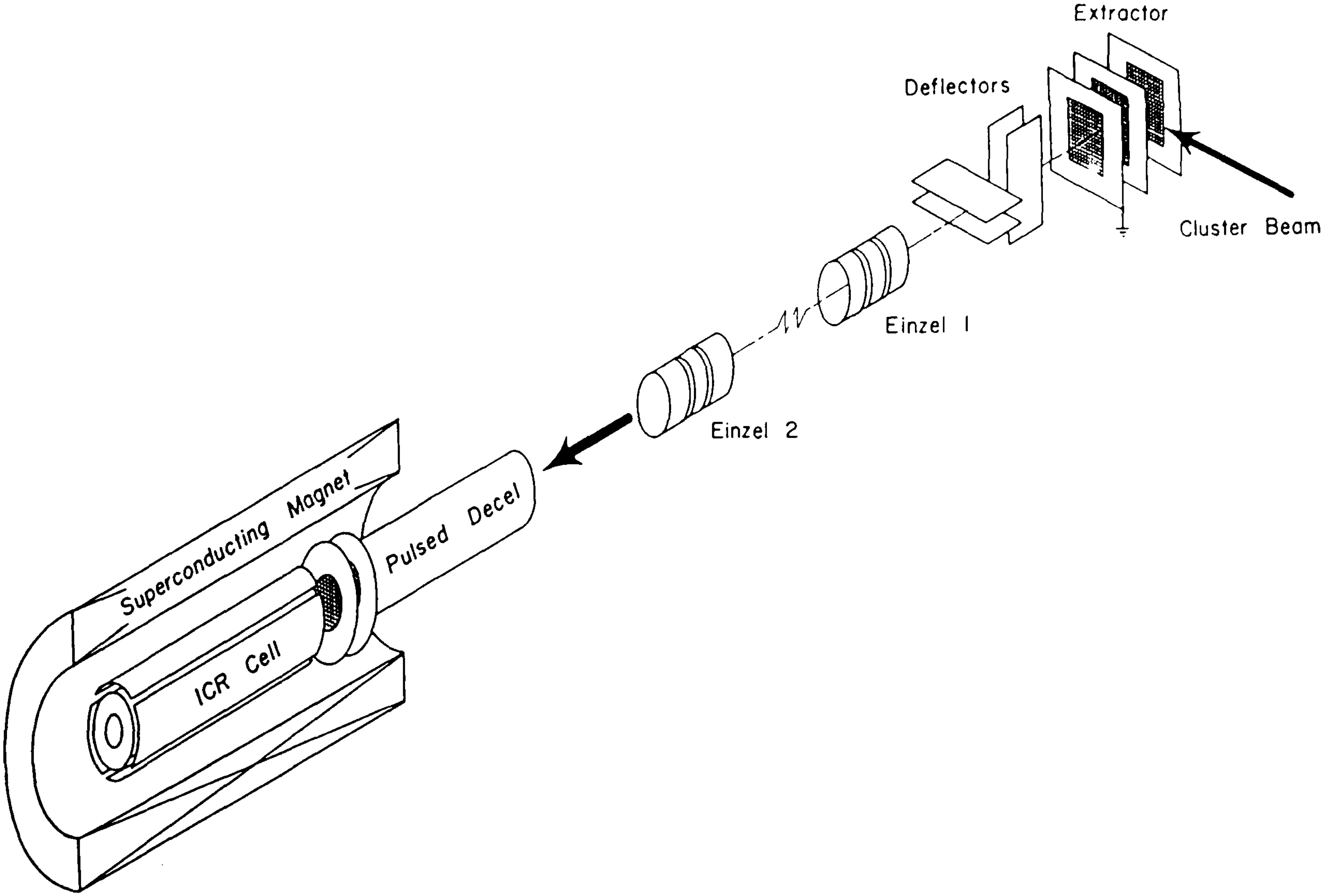
Figure 2. FT-ICR mass spectral study of the chemisorption activity of mass-selected silicon clusters to ammonia. The top panel shows the initial mass distribution prior to exposure to ammonia, the bottom panel shows the mass spectrum after exposure to 4×10^{-7} torr ammonia for 4 seconds.

Figure 3. The Kaxiras proposal for the most stable structure of the specially stable and unreactive cluster, Si_{45}.

Figure 4. FT-ICR mass spectral study of the chemisorption activity of silicon clusters to ethylene. The top panel shows the initial mass distribution prior to reaction, the bottom panel shows the markedly different pattern obtained after exposure to 1×10^{-5} torr ethylene for 60 seconds.

Figure 5. Demonstration of laser annealing of silicon clusters levitated in the ICR trap. Top panel: the result of reactions with ethylene on Si_{39}^+ and Si_{45}^+ as injected from the supersonic beam source. The $Si_x(C_2H_4)_y^+$ reaction products are labelled with the symbol "E_y". Bottom panel: result of the same extent of reactions on Si_{39}^+ and Si_{45}^+ after annealing with 30 pulses of XeCl laser radiation at 1 mj cm^{-1} $pulse^{-1}$.

Figure 1



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Deflectors
Cluster Beam
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Einzel 2
Pulsed Decel
Superconducting Magnet
ICR Cell

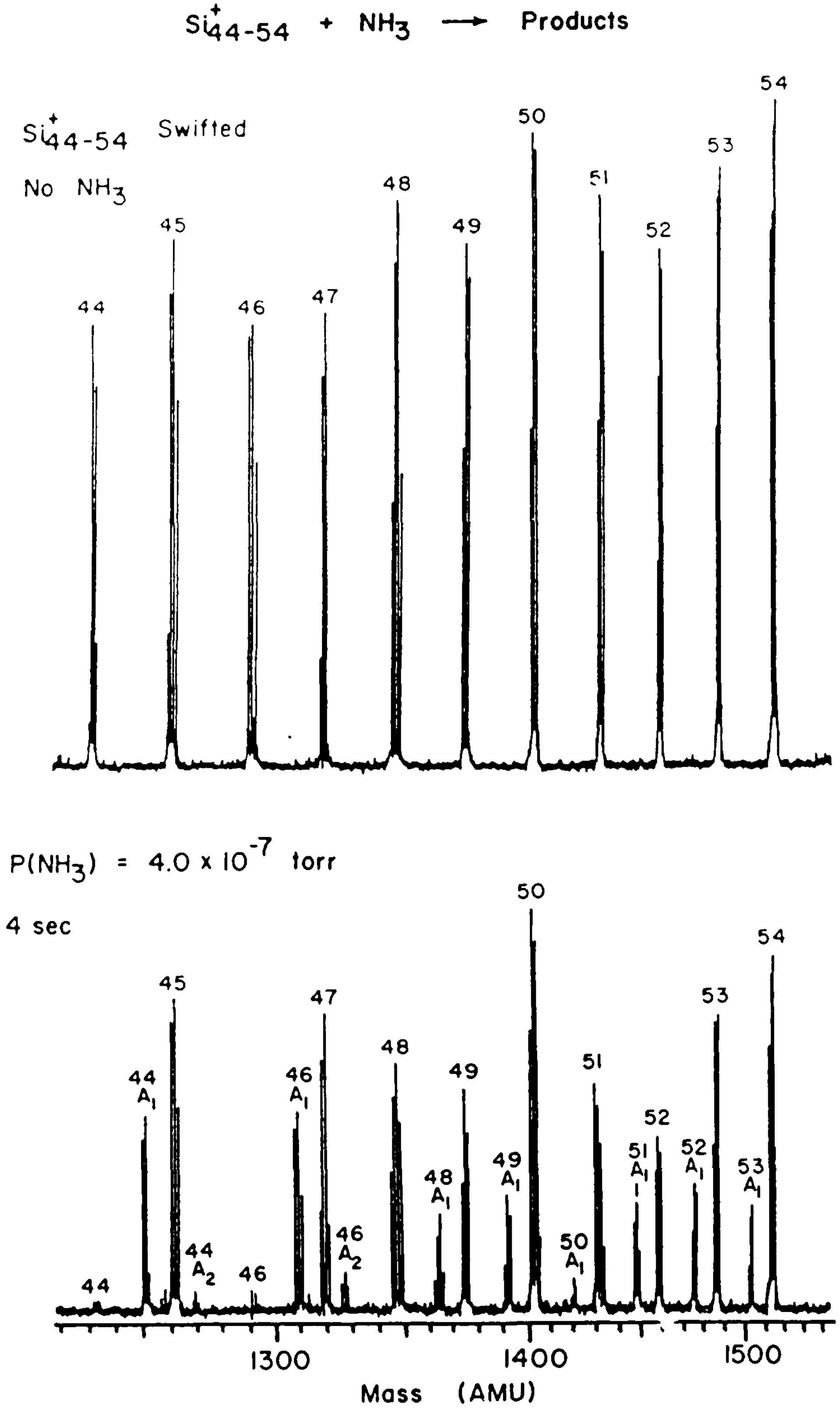
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Figure 3

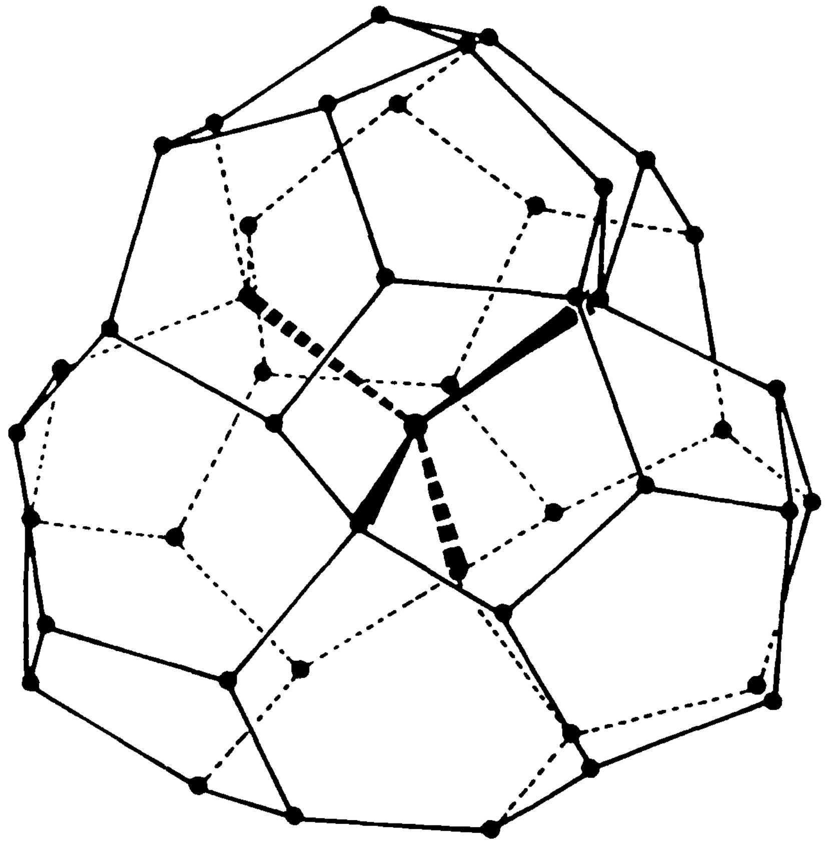
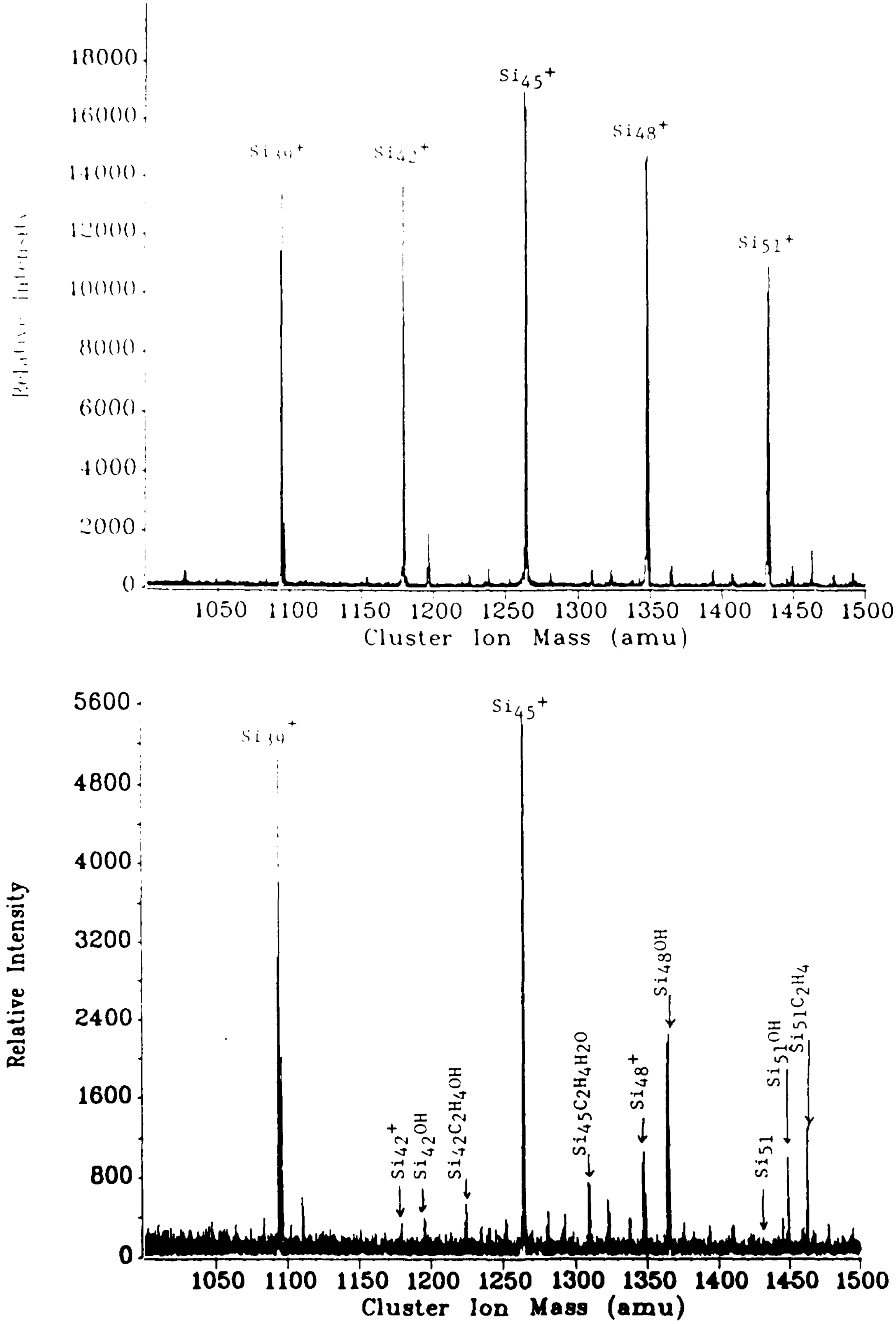


Figure 4



Relative Intensity
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16000
14000
12000
10000
8000
6000
4000
2000
0
Si_{39}^+
Si_{42}^+
Si_{45}^+
Si_{48}^+
Si_{51}^+
1050 1100 1150 1200 1250 1300 1350 1400 1450 1500
Cluster Ion Mass (amu)
Relative Intensity
5600
4800
4000
3200
2400
1600
800
0
Si_{39}^+
Si_{45}^+
Si_{42}^+
$Si_{42}OH$
$Si_{42}C_2H_4OH$
$Si_{45}C_2H_4H_2O$
Si_{48}^+
$Si_{48}OH$
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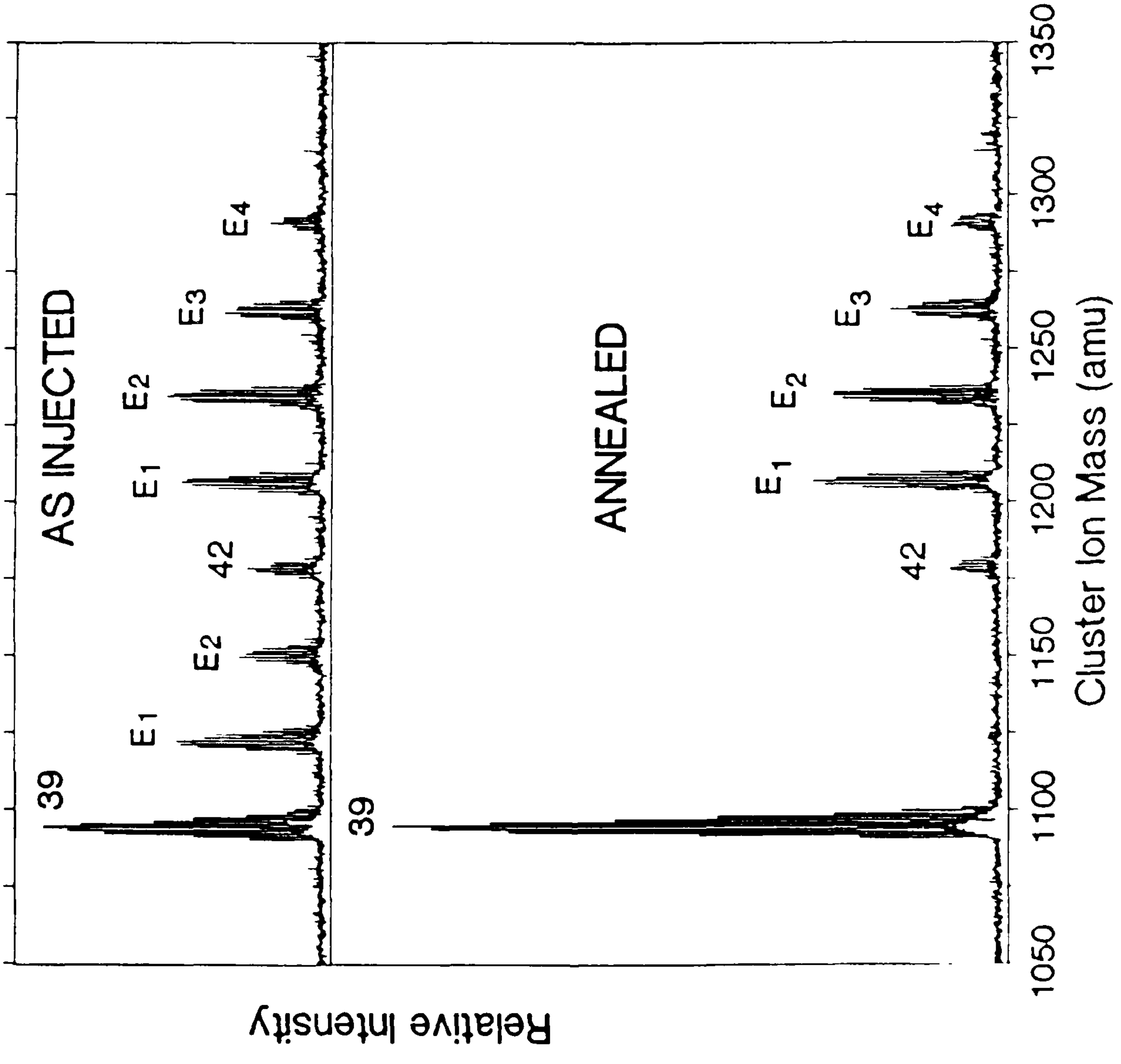
Cluster Ion Mass (amu)

Figure 5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