DON E. HARRISON, JR. A RETROSPECTIVE AND PROSPECTIVE

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This review is dedicated to the memory of Don Harrison. We first met Don in September of 1977 at the idyllic surroundings of the Naval Postgraduate School. There were several motivations for seeking him out. It appeared that the SIMS technique would achieve enormous popularity because of the emerging applications to the semiconductor industry, to surface science and to microscopy. On the experimental side, however, there were frustrating problems. Secondary ion yields could not be utilized in any quantitative sense to get at concentrations. The origin of the mass spectra themselves was extremely unclear. Only a few groups were attempting well–defined experiments in ultra–high vacuum on single–crystal targets. On the theoretical side, handwaving was all the rage. The relationship between the nuclear motion subsequent to the ion–bombardment event and the electronic excitation mechanisms was unclear. Only cartoons could be used to describe the tantalizing formation of molecular ions.

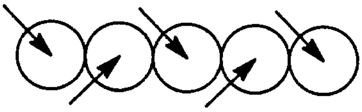
As turned out, our Chairman Drew Evans, alerted us to several articles by Harrison and his students involving the computer simulation of sputtering. As the theoretician of this duo, Garrison had just completed one of the largest quantum mechanical calculations to date (on rotational cooling of formaldehyde) and could immediately recognize the simplistic elegance of Harrison's methods. As an experimentalist, Winograd quickly saw that these calculations could be performed on targets that he could study under well–defined conditions in his own laboratory.

Our initial discussions here in Monterey with Don were quite discouraging. We found out that he had been thinking about sputtering for more than 20 years. In retrospect, however, it is clear that at that time he had the clearest cerebral images of this process of any living being. Yet, he did his best to convince us that it was a dead field. He ticked off the difficulties. It was impossible to construct potential functions that were sufficiently accurate to provide realistic numbers for the chemical systems we were curious about. Computers were too small to crank away on microcrystallites that were large enough. Moreover, Don's teaching responsibilities were time–consuming, he had no grant money and he did not have access to graduate students or post–docs. In short, he told us to forget it. And yet, we felt a sense of enthusiasm building within him that said maybe this is the right time to forget about all the reasons for not continuing and just forge ahead.

Virtually every model of sputtering utilized the binary collision approximation (BCA). In this approximation it is assumed that each target atom generates one secondary collision cascade in which energy is shared by a series of collisions. Next, it is assumed that the collisions themselves occur only between two atoms at a time. In his Ph.D. thesis work during the early 1950's, Harrison realized that the transport theories of sputtering relied heavily on the BCA, noting in his very first publication "... in all probability the binary collision requirement made in the development of that (transport) equation is not met in the problem under consideration."[1] No analytical theory could avoid the BCA. By 1960, however, Vineyard and his group at Brookhaven developed a computer code to model radiation damage in alkali halide crystals without the usual approximations.[2] Encouraged by these results and discouraged by his own efforts to develop explicit mathematical relationships, Harrison took the Vineyard approach, modified it to simulate sputtering and our first glimces into the detailed nuclear motion were created.[3] For those fortunate enough to know Don well, you know that he had a certain irrascible style. It is fascinating that he concluded that important first paper with "A detailed analysis of our results has not produced any startling conclusions."

During those early years, there were two particularly significant concepts which arose from the calculations, both of which depended critically on the ability of the computer simulations to provide an atomistic picture of the lattice dynamics. First, Harrison was able to explain the origin of the angular anisotropies observed from single–crystal targets.[4] With the early computers available to him, he was not able to obtain results directly comparable to experiment. His calculations relied on microcrystallites containing just 100 or so atoms. He could only afford to sample a few dozen ion impacts on the target, and the effort required weeks of computer time. For comparison purpose, we now routinely use 2000 atom crystallites and obtain ~4000 trajectories in order to obtain experimentally observable numbers. Despite this drawback, however, he could clearly follow the flow of momentum through the close–packed rows of the solid and could obtain angular distributions of desorbed atoms with the same symmetry as those found by experimentalists.

A second important discovery involved the mechanism of the sputtering of clusters. This issue was relevant to the SIMS community during the mid–1970's since many labs, including our own, were interested in using the molecular information in the mass spectra to study surface chemical reactions. Earlier work on the sputtering of neutral K_2 suggested that recombination of atoms not originally bonded together was important.[5] If true, there would not be a simple relationship between observed molecular ions and surface species. With computer simulations, Harrison could examine the trajectories of all of the atoms desorbing from a single ion–impact. He could then make some guesses about the forces between these atoms to see if reaction occurring *after* desorption was possible. As we have said, Harrison could follow the flow of momentum down close–packed rows via his so–called "up–down" mechanism as



For atoms in a metal, he reasoned, it would be virtually impossible for near–neighbor atoms to eject as dimers since they are inherently moving in opposite directions. He provided the clearest evidence for recombination in molecule formation and sent the rest of us scrambling to simplify the mess. As it has turns out recombination is certainly a factor in the ejection of cationized or protonated molecules, although for systems where the intramolecular forces are stronger than the intermolecular forces, it is clear from experiment and computer simulations[7] that direct molecule emission is feasible.

In our first interaction with Don, he literally gave us all of his computer codes on punched cards. Although the objective was to extend his original ideas to provide measurable numbers on more complicated systems, our first effort really involved a repeat of some of his earlier simulations on the bombardment of the 3 primitive crystal faces of Cu by 600 eV Ar^+ ions.[8] At that time, we were on leave at the University of California at Berkeley. Our host, Professor Dave Shirley, generously provided us with access to a CDC 7600 computer which, at the time, was one of the world's best. This gave us the opportunity to greatly expand the scope of the original Harrison calculations.

From an experimental point of view, the results were indeed jarring. We could literally feel the violence associated with the ion/solid event as the trajectory data came spewing forth. From the printouts, however, it became obvious that there were key experiments one could perform to test the reliability of the simulations. More importantly, the angular distributions that we calculated suggested that it might be possible to say something about the bonding geometry of overlayer atoms on single–crystal surfaces.[9] The desorbing atoms were found to be mostly originating from the first layer and were found to be strongly channeled or blocked by other surface atoms. Hence, surface structural information not obtainable by other techniques seemed within reach.

The trajectory data – be they qualitative or quantitative – forced the community to think about the SIMS process on a more atomic level. Using Harrison's program and the advanced graphics capabilities of the computer center at Lawrence Berkeley Laboratory, we produced a short movie, "Close Encounters of Another Kind", which vividly represented these processes. They also impressively verified Don's 1956 pronouncement that the BCA was suspect. The movie clip was full of pictures of simultaneous interactions between many atoms. All of these developments raised his spirits, his enthusiasm for science as well as his federal funding level. It was a pleasure to be a part of it all.

Our collaboration continued as we returned from California to take–up new research opportunities at Penn State. It was possible to construct a SIMS machine with the capability of measuring secondary ion yields as a function of energy and angle using a movable quadrupole mass detector.[10] The experimental results were in remarkably good agreement with Harrison's predictions. In addition, by examining the angular distributions of Ni_2^+ relative to Ni^+, we could confirm that recombination of next–nearest neighbor Ni atoms was occurring in the sputtering of Ni{001}.[11] We used the channeling and blocking idea to locate the binding site for oxygen atoms on Cu{001} and could even estimate the magnitude of the image interaction between the departing ion and the metal surface.[13] All seemed well.

Don Harrison, although now very supportive, remained skeptical. The best one could do experimentally on single crystals was to detect the secondary ions directly. There was no known way to make the analogous measurement on the neutral species with sufficient sensitivity to avoid surface damage. The classical dynamics computer simulations, of course, ignored the effects of electronic excitations and ionization. Was it valid to use his code to predict SIMS trajectories? He often challenged us to discover a way to find out. During the spring of 1981, we felt that multiphoton resonance ionization (MPRI) of neutral species above the surface could provide adequate sensitivity to yield neutral trajectories. After several years of construction, a dedicated group of students completed an imaging detector which allowed energy and angle–resolved neutral (EARN) distributions to be obtained with high precision.[14] By 1986, we had obtained a complete set of data from Rh{111}.[15]

Since the early years, the computer revolution moved into full swing. Harrison's models could now be expected to yield accurate answers. With our new data, however, a few nagging difficulties refused to disappear. The computer simulations could not reliably reproduce the angle integrated kinetic energy distributions of the neutral component (see Fig. 1), regardless of how all of us adjusted the parameters of the pair potential function. It was during a second visit to California, this time at Caltech with Tom Tombrello, that we traced this difficulty to the use of pair–potentials. These types of potentials, where the interaction between two atoms is independent of the presence of a third atom, was ubiquitous in all types of computer simulations for liquids and solids. Our problem was that at the interface between the solid and the vacuum, the number of nearest–neighbors of the desorbing atom is changing rapidly. The pair–potential description is particularly bad under these circumstances. Although the angular distributions compared well with experiment, this problem created difficulties with the calculated velocity distributions.

Fortunately for all of us, a group at Sandia Livermore was developing a many–body potential function using the embedded–atom–method (EAM).[16] In Don's last collaboration with us, we were able to incorporate the EAM forces into his formalism. After some struggles between the east and west coast, we found a nearly perfect fit between the EARN distributions and the classical dynamics computer simulations.[17] The results are summarized in Fig. 1. The problem was solved.

Particularly during the last 10 years, Harrison and his collaborators have contributed greatly to the visualization of the ion/solid interaction event. His methods have led to a greater appreciation of the damage that the incident particle creates in the lattice. True to his form of trying to calculate quantities that are ultimately measurable, his calculated shape of surface pits[18] has recently been observed directly with the scanning tunneling microscope.[19]

What is Don Harrison's legacy to science in general and to the SIMS community in particular? His pictures of the ion/solid interaction have certainly been the inspiration behind many of the experiments performed in the past and those planned for the future by our group. Computer simulation of the dynamics of solids is now a hot topic, in part due to bigger computers and in part due to the development of realistic, many–body potential functions which accurately describe complex materials. Harrison's basic goals for sputtering will soon be extended to the study of much more complicated materials such as Si,[20] GaAs or perhaps even large organic molecules and proteins. The time is ripe now to attempt ever more ambitious projects involving thin film growth (molecular beam epitaxy[21]) and reactive ion etching.[22] In SIMS, we are mainly concerned with the creation of secondary ions. Regardless of which mechanisms are responsible for this creation, we know that the Newtonian processes underlying ion bombardment must be considered. Thanks largely to Don Harrison, we all have a much clearer view of this important dynamics. In our opinion, he was a man ahead of his time who lived long enough to see many of his ideas come to fruition. He will be missed.

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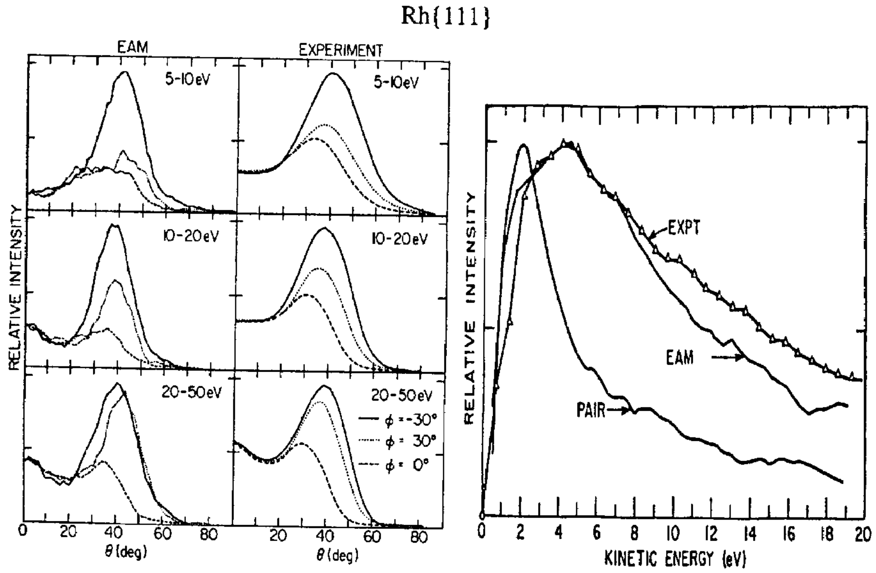

Fig 1. Comparison between computer simulated and experimental angular and energy distributions. The angle θ refers to the polar angle of detection measured with respect to the normal. The angle φ = 0° indicates the close-packed azimuthal direction, while φ = ±30° refers to the two open directions.[17]