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## Early example of an interdisciplinary approach in industry: Harold F. Winters's contributions

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## Early example of an interdisciplinary approach in industry: Harold F. Winters's contributions

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Harold was one of the key pioneers who brought rigorous surface science approaches to bear on a variety of phenomena related to plasma–surface interactions encountered in contemporary plasma technologies such as physical and reactive thin film sputtering, reactive ion etching (RIE), ion implantation, and gas gettering but also in diverse areas such as the design of thermonuclear reactors and estimation of drag on spacecraft.

From a historical point of view, it might be useful to recall how an **interdisciplinary** approach evolved in an **industrial** environment at a time when this was not yet all that fashionable and how Harold's basic science approach greatly contributed to the efficacy of this approach. Materials Science as a discipline was very much in its infancy in the late 1950s.

In early 1958, one of us (E.K.), trained as a physical chemist, was the seventh professional member to join the newly established IBM Research Division Laboratory on the West Coast. The other six members consisted of a linguist, a psychologist, a fluid dynamicist, a mathematician, a solid state physicist, and a physics theorist. E.K. was given 6 months to come up with a research plan of how his chemistry background might seed an effort that could eventually impact IBM's evolving technologies, which at that time centered around magnetic recording and electro-photography at the already existing IBM applied lab and manufacturing facilities in San Jose, CA.

After extensive discussions with key people, it became clear that achieving much higher magnetic storage density and exploiting potentially much faster magnetization reversal mechanisms will require the ability to produce both the magnetic storage and the read/write transducer media in a very **thin film** form.

The magnetic storage medium that was used in the first "Random Access Hard Disc Drive," introduced by IBM in 1956 in San Jose, was a 1000 nm thick magnetic paint applied by a centrifugal spinning process onto 28 in. hard Al disks. The magnetic media consisted of ferromagnetic, acicular gamma Fe<sub>2</sub>O<sub>3</sub> grains suspended in a polymeric fluid matrix. However, producing far more concentrated, very much thinner uniform magnetic layers over large areas was deemed unrealistic using this centrifugal spinning process. It was already understood why the desired magnetic

characteristics of this storage medium critically depended on having the correct stoichiometry, a specific allotropic crystallographic phase, and size and shape of the magnetic particles. The magnetic media in the read-write heads at that time centered around multicomponent ferromagnetic metallic alloys, e.g., NiFe, Permalloy, where desired magnetic properties, e.g., low magnetostriction, were known to critically depend on the right ratio of Ni to Fe.

Electrochemical plating or alternatively thermal vaporization or chemical vapor deposition approaches were seriously considered but, at the time, deemed less than ideal for a variety of reasons. An extensive literature search led to an alternate possible approach which, at least in principle, had the potential of fulfilling many of the microscopic material requirements using a "**low temperature**" process capable of depositing thin layers of a **large** variety of materials uniformly over a large substrate area, namely, "Glow Discharge Sputter Deposition."<sup>1</sup> In the context of various other thin film applications emerging at the time, the prospect of being able to work at relatively low temperatures was considered a real potential asset especially in multilayered thin film assemblies where interfacial issues such as interdiffusion can be expected to play an important role.

From a material's point of view, an emerging concept, among several at the time, about the mechanism whereby sputtering takes place was that it occurs as a result of a binary momentum transfer collision between an energetic incident ion and a **cold** target atom, giving rise to primarily **atomic** sputtered species with a non-Maxwellian distribution of energies in the **1–10 eV** range. The sputtering ratio between a given incident gas ion and a variety of elemental target materials as a function of incident ion energy over a large energy range was already well known. A sputtering approach promised to alleviate some of the key problems inherent in **high** temperature processing involving thermal vaporization. This was expected to be especially true for multiconstituent alloys and compound targets where large elemental vapor pressure differences in alloys and thermal dissociation problems in compounds are often inevitable. However, whereas it was clear that eventually being able to synthesize multiconstituent materials should be possible in reactive glow discharge environments applying conventional ground state chemistry may well be of little value since unknown free radical species in various states of excitation were as yet largely unknown especially in reactive plasmas.

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For someone (E.K.) trained in high temperature equilibrium thermodynamics and kinetics, this was viewed as a real exciting challenge. It was also already clear that control over the composition and the structure at a *microscopic* level of the resultant thin film on a substrate was critical, if control over any and all *physical* properties, like magnetic, optical, electrical, and mechanical, are to be realized.

In the context of the particular ferromagnetic materials being considered at the time for storage media, such as iron oxides, getting the right allotropic form, e.g., gamma  $\text{Fe}_2\text{O}_3$  versus alpha  $\text{Fe}_2\text{O}_3$ , was critical since one is ferromagnetic and the other antiferromagnetic. In the case of rare earth garnets, e.g.,  $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ , being considered in the context of magneto-optical storage, getting the Fe cations which are present in two oxidation states in this material, into the right tetrahedrally and octahedrally coordinated interstitial lattice sites within the oxygen lattice, was important. Only if this can be accomplished will the key magnetic property, the compensation temperature, where the antiferromagnetic magnetic coupling of the two magnetic sublattices takes place, result in zero magnetization at room temperature. This was an essential requirement for magnetization switching purposes of this material as a storage medium at ambient temperature. This kind of critical interplay between compositional and structural characteristics with the resultant magnetic properties made it very clear early on that making very careful physical property measurements such as the magnetic compensation temperatures can help to give answers to important structural and compositional questions that were extremely difficult at the time to be resolved by standard analytical procedures. This serves as a good example of the value of an interdisciplinary material science approach.

Our first goal was to build and explore appropriate sputter deposition configurations suitable for *rapid* deposition of magnetic metal and alloy thin films.<sup>2,3</sup> To optimize deposition rates, our work included a study of “Magnetic Field Effects on a Coplanar Abnormal Truncated DC Glow Discharge and their relation to Sputtered Thin film Growth.”<sup>4</sup> We also explored Efficient *Low* Pressure Sputtering both in a “Large Inverted Magnetron Suitable for Thin Film Synthesis”<sup>5</sup> and a “Supported Triode Sputtering configuration.”<sup>6,7</sup> Exploring the last two options was partly motivated by our desire to work in longer mean free path environments, thereby reducing the as yet largely unexplored multifaceted collision processes within the *higher* pressure plasma regimes. This also allowed us to compare more meaningfully what we were learning about the nature of surface sputtered particles from both metals and alloys and metal oxide targets in our parallel studies using a 1–10 keV duoplasmatron inert gas ion beam source for sputtering and *in situ* electron beam induced electronic excitation of the sputtered species, leading to characteristic optical emission and subsequent species identification.<sup>8,9</sup>

By early 1962, Kay felt qualified to publish an extensive review chapter of key factors relevant to thin film growth by sputtering in a glow discharge environment.<sup>1</sup> He entitled this book chapter as “Impact Evaporation and Thin Film Growth in a Glow Discharge” in *Advances in Electronics and Electron Physics*, Vol 17, 1962, naively thinking that the

term “Impact Evaporation” may more meaningfully describe what is going on at the sputtering target. “Sputtering” seemed to be such a nondescript interpretation of “Kathodenzerstäubung,” the title originally given to the phenomenon in Germany in the middle 1800s. In hindsight, this attempt to change the nomenclature turned out to be totally futile. The term “Sputtering” was here to stay.

By the middle 1960s, it also became abundantly clear that in order to eventually understand nucleation and film growth on a substrate held in a plasma, it will inevitably be necessary to know not only how and why chemical species leaving a *cold* target by sputtering are chemically, energetically, and directionally different from those produced by thermal vaporization but also what specifically happens to these sputtered species in transit across the plasma in different mean free path regimes, where several other types of collision processes were going on. Most importantly, we needed to know how do all these processes affect what was going on at the *plasma-substrate* interface and its immediate environment. This would require the definition of parameters such as the types, energy, and direction of *all* species arriving *at the substrate*. In contrast to already existing studies of nucleation and growth processes involving thermal vaporization and condensation of metals in a *high vacuum* environment, very little was known along similar lines in the higher pressure plasma environments and certainly little definitive about any synergistic effects in such a complex environment.

Most of our early insight into sputtered thin films in a plasma were based on phenomenological observations, resulting from carefully changing voltages, pressures, gases, and substrate temperature in different discharge configurations and by correlating their effects on the structure and composition of the resultant film and its physical properties, such as magnetic, optical, and electric.<sup>2–14</sup> Obviously, plasma diagnostics and radiation enhanced surface science talents were called for.

Adequate answers to our *in situ* plasma questions were not available to us until Harold F. Winters (H.F.W.) in 1963 and John W. Coburn (J.W.C.) in 1968 joined our group. Between them, over time, they upgraded our understanding of what was going on in our various discharge environments by an order of magnitude. J.W.C. built an elegant “System for Determining Mass and Energy of Particles Incident on a Substrate in a Planar Diode Sputtering System” as well as upgraded our insight into plasma potential in discharge systems run in different frequency modes as well as in supported triode discharges.<sup>15–19</sup> The use of these plasma systems provided many new insights into our ongoing plasma thin film work.<sup>20–31</sup>

H.F.W.’s former background was especially useful to our need to understand physical and chemical surface *sorption* phenomena in the presence of various forms of energetic incident irradiation. His Ph.D. thesis (1963) and initial studies at IBM dealt with “Adsorption resulting from electron impact on gas phase molecules,”<sup>32–38</sup> which to us had important implications to both the physical and reactive sputtering environment in our plasmas. Harold also conducted the first systematic experimental investigation of physical sputtering

of a chemisorbed gas from a surface in an UHV environment.<sup>39</sup> He showed that sputter yields were unexpectedly large and that the energy dependence deviated from that observed for elemental materials. He also developed an important collisional model with Peter Sigmund that suggested that direct collisions between the incoming and outgoing ions and the adsorbed gas were important processes leading to sputtering.<sup>40</sup> These results were quite consistent with earlier results we obtained indirectly from large sputtering yields of most chemisorbed gases in reactively sputtered films in RF plasmas as well as in deliberately substrate biased glow discharges.<sup>41</sup> In a different study, Harold also discovered that there was a large isotope effect<sup>42</sup> associated with the dissociative chemisorptions of certain low molecular weight hydrocarbons. He interpreted his data as indicating that the reaction was completely dominated by quantum mechanical tunneling of hydrogen through a potential barrier.

In our group's parallel *plasma* sputtering studies, we were making a variety of observations indicating that not only the morphology and crystallographic orientation but also the unit cell lattice parameters and defect structure of sputtered metal films deposited on an electrically well *grounded* substrate in DC discharges were significantly changed depending on which *inert* gas (Ar, Kr, and Xe) was being used to sputter the highly negatively DC biased metal cathode target in different pressure regimes.<sup>30</sup> As expected, these structural changes in the films were also reflected in very significant ways in their resultant physical properties<sup>14</sup> and therefore emerged as an important issue for thin film growth by sputtering in discharges in general, as used in those early days. We later studied these structural changes due to energetic particle bombardment in much greater detail.<sup>25,26,31</sup>

All this suggested that somehow species with sufficient kinetic energy to cause even crystalline lattice deformations are bombarding the electrically grounded film surface causing some of these structural changes. Presumably, none of the high energy *positively* charged incident noble gas ions can be backscattered as *ions* from the highly negatively biased cathode target surface across the steep field gradient of the Crookes Dark Space. Such alternatives as energetic 1–10 eV *neutral* sputtered metal target species or secondary *negative* metal ion emission from the target or electronically excited, long lived energetic metastable Ar\* and their ability to Penning ionize metal atoms while traversing the plasma<sup>17</sup> were carefully considered as possible energy sources that might influence the nucleation and growth process and structural features observed in our films. Pressure dependent mean free path considerations as a “thermalizing” process of these species crossing the plasma were carefully taken into account.<sup>30,44</sup>

Initially, energetic (1–10 eV) sputtered neutral atoms arriving at the substrate were considered as the most likely source for some of the observed structural film features,<sup>30,31</sup> possibly due to unfamiliar energy enhanced surface diffusion processes and/or the creation of novel nucleation sites, although being responsible for unit cell lattice distortions

seemed somewhat far fetched in the 1–10 eV energy regime. Discussions with Harold saved the day by alerting us to the likelihood that the backscattered much higher kinetic energy *neutral* noble gas atom from the cathode target was very likely a result of Auger neutralization of the incident *high* energy noble gas ions at the negatively biased cathode target. He estimated that as much as 60 eV/Ni atom arriving at the substrate was reasonable in the voltage and pressure regime in which we were working. This insight has since been used by many investigators to explain numerous phenomena both in and out of plasma environments.

A further question immediately arose: was it likely that these *energetic* noble gas atoms not only change the film growth process and subsequent film structure but are also actually permanently trapped in the thin film during film growth at room temperature? Harold produced convincing evidence that this is certainly not likely by either *ground state* physisorption or chemisorption at room temperature. Harold also immediately developed an elegant laser induced flash evaporation technique followed by mass spectrometry for quantitative gas analysis in films, which allowed us to show unequivocally that inert gas was in fact embedded throughout the sputtered film.<sup>43–45</sup> Earlier surface sensitive escape depth limited electron spectroscopy for chemical analysis and Auger spectroscopies were misleading since they never showed us any evidence of trapped noble gases in the top few monolayers of the film. Obviously, this extensive gas trapping insight as described became crucial when *deliberate* negative substrate *biasing* with respect to the plasma potential became the standard procedure for bombarding the growing film in a variety of DC and RF plasma configurations in order to deliberately manipulate the microstructure and resultant physical properties of the thin film.<sup>24–28</sup>

Throughout his career, Harold recognized the need for accurate fundamental cross-sections for some of the key collision processes relevant to many of the areas mentioned above. Early on, he had developed a method<sup>32</sup> for measuring the total electron impact dissociation cross-section for many of the gases used in material processing. Most of the cross-sectional data in the literature were provided by these experiments.<sup>32–38</sup> In particular, this dataset is widely used as input for the modeling for reactive gas discharges.

Harold's work on sorption phenomena on well defined crystalline surfaces indicated among many other things that sorption of incident ground state *molecular* oxygen and nitrogen does not occupy all available sites on the surface at saturation coverage. This stimulated an attempt in a parallel project by E.K. to possibly overcome this problem using plasmas. This was particularly relevant in possibly overcoming critical stoichiometric oxygen deficiencies in important insulating, transparent metal oxide films such as ZnO and SnO<sub>2</sub>. The fact that ZnO was also an excellent photoconductor was of special interest to us in the context of potential applications in electro-photography. All ZnO prepared in nonplasma environments always led to ZnO with dark resistivities orders of magnitudes lower than those estimated from the ZnO bandgap of 3.37 eV. This was considered most likely to be due to a very small oxygen deficiency in the



ZnO lattice. Enhancing the availability of oxygen **atom** radicals and ions from several possible sources<sup>17,23</sup> in a rf plasma and their potential for enhanced sorption possibilities was explored, and dc dark resistivities of ZnO were indeed enhanced by many orders of magnitude.<sup>13</sup> However, the subsequent photoconductivity in the presence of light irradiation was drastically reduced, which, of course, was very discouraging in the context of electrophotographic applications where high resistivities in the dark are required to hold an electrostatic charge and then having a high photoconductivity when irradiated with light is critical to the formation of an image.

The low photoconductivity found was thought to be due to the introduction of as yet unknown structural defects produced by the plasma treatment. Detailed AC conductance and capacitance electrical measurements in different frequency regimes revealed how band and hopping conduction played a key role in these high resistivity ZnO films and led to the conclusion that the high resistivity is due to a compensation of oxygen vacancies on regular lattice sites by oxygen on interstitial sites. The deep traps formed in this way capture most of the free electrons generated by defects and impurities. The large activation energy of the trapped electrons is then thought to be responsible for the high resistivity observed at room temperature.<sup>14</sup>

This serves as yet another example where an interdisciplinary approach gave us new insights that helped us to evaluate the efficacy of this plasma approach as a viable solution to an important need in electro-photographic applications.

In later years, Harold *et al.* provided much of the available data on how **energy**<sup>46–49</sup> is transferred to a solid lattice by ion bombardment in the 0–4000 eV range as a function of ion mass, target mass, and incident ion energy. These studies provide detailed rigorous insight into these energy transfer processes in this energy range. Obviously, these data were used by us to provide additional insight into processes which occur at sputtering targets as encountered, for example, in analytical depth profiling using ion bombardment. So, for example, J.W.C. and E.K. developed a model that showed how the interpretation of depth profiling<sup>50</sup> by sputtering measurements was strongly influenced by the altered chemical composition at the surface generated as a consequence of ion bombardment of multicomponent targets.<sup>50–53</sup>

By the middle 1970s, Harold's interests shifted by the great need for much higher spatial resolution etching procedures in the Si/SiO<sub>2</sub> integrated circuit structures for semiconductor electronic transistor applications. Perhaps one of the most important contributions in terms of the overall impact by Harold Winters with John Coburn has been in the area of plasma assisted **etching** with particular emphasis on developing a detailed understanding of physical and chemical mechanisms.<sup>54–60</sup>

For an overall review of this work, see Ref. 60.

To facilitate these studies, they demonstrated that etching can be achieved **outside** the plasma by using XeF<sub>2</sub> gas as a reactive gas source of F atoms. They developed experiments to simulate plasma processes by using directed beams of reactive gas, ions, and electrons. Modulated beam mass

spectrometry was used to measure the etch products, reflected incident species, and reaction by-products. XPS and Auger spectroscopy were used to understand surface conditions. These directed beam experiments were very helpful in providing a qualitative understanding of the complex phenomena occurring at surfaces in reactive gas plasmas.

One of the early key sets of results by Coburn and Winters using either ion or electron beam surface radiation was a clear, **unequivocal** demonstration of how and in what systems (Si, SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, and SiC) radiation-enhanced surface chemistry leads to a large increase in etching rates, which is the critical ingredient for selective and directional etching in technological applications.<sup>61–68</sup> For key reviews of this work, see Refs. 55 and 60. This beam work was the forerunner of ion-beam assisted chemical etching applications involving both broad and finely focused ion beams. They also demonstrated the role of carbon and carbonaceous polymeric materials in the previously discovered selective etching of SiO<sub>2</sub> and in etching directionality by means of sidewall passivation as encountered in then commonly used CF<sub>4</sub> (Ref. 69) etching plasmas. They also pointed out the role of feature conductance in high aspect ratio etching and have also developed a model to explain the influence of doping on etching.<sup>68</sup>

Another example of an interdisciplinary approach in our group was the theoretical work by one of our quantum chemists, Bagus *et al.*<sup>70,71</sup> These studies were again inspired by Harold Winters's experimental work related to chemisorption and subsequent surface penetration issues arising in the interaction of halogens with Si contrasted with the then already widely studied interaction of H with Si. One key question was why F atoms could spontaneously etch Si, while Cl atoms could only be effective in etching Si if the surface was simultaneously subjected to energetic particle bombardment. Bagus presented the results for the Si-F electronic structure based on a cluster model representation. This molecular orbital cluster model uses *ab initio* quantum chemistry to determine accurately the local as opposed to the extended (band structure) contributions to the adsorbate–substrate interaction and bonding. Their work showed that F atoms can penetrate into the Si lattice by going over a relatively small barrier of ~1 eV, whereas the barrier for Cl penetration is ~13 eV.

Since surface penetration is key to the formation of volatile Si-halogen compounds, the theory explains why F atoms can spontaneously etch Si, while Cl atoms cannot. The physical explanation is that there is a size effect where the smaller F(-) anion can penetrate the surface, while the larger Cl(-) anion cannot. This explanation led to a puzzle about why H, which is obviously smaller than either F or Cl and which chemisorbs above the surface, does not penetrate spontaneously. They explain this finding by showing that H forms a covalent bond with Si, while F and Cl are anions which are attracted to the Si surface by electrostatics.

In addition to the areas mentioned above, Harold, in ongoing discussions, gave us invaluable input about contemporary surface science issues in a variety of studies on

synthesizing novel materials prepared in complex plasma environments. One example was our extensive study on composite granular thin film materials, involving the controlled growth of metal nanoparticles from sputtered metal atoms in a chemically inert plasma polymerized thin film matrix. Our approach involved utilizing simultaneous high energy physical sputtering of metals at the cathode and fluorocarbon plasma polymerization at the substrate in a rf driven plasma environment. Using various ratios of injected inert gas to low molecular weight, volatile fluorocarbons allowed control over the volume fraction of metal in the polymer. The key chemical species in these fluorocarbon-argon plasmas are energetic Ar ions, F atoms, and unsaturated  $(CF_2)_n$  radicals.<sup>72-74</sup> Several competing surface reactions in these rf driven plasmas take place simultaneously at all surfaces in contact with the plasma, and these surfaces are subject to different degrees of ion bombardment depending on their potential with respect to the plasma potential. The energy of ions and type of species<sup>73</sup> arriving at a particular surface in these systems and the surface temperature determine whether sputtering and reactive ion etching or polymerization will dominate at that surface.<sup>74,75</sup> The connection of this overall approach to the ongoing studies of Harold's and John's fluorocarbon related, RIE and studies of the role of carbonaceous materials in sidewall protection is self-evident.

Electrical and optical properties<sup>76-80</sup> of these granular metal containing polymer materials above and below the onset of percolation were of particular interest to us in the context, for example, of fine line laser induced circuit writing in air without the need for elaborate lithography.<sup>81-83</sup> These films can thus be built up into a three-dimensional structure with metal lines and/or vias, making this a very versatile potential approach for microelectronic circuitry or packaging applications.

From a material-science point of view, the feasibility of this approach hinged on demonstrating that photoablation using a scanning excimer laser allows the removal of the highly cross-linked plasma polymerized fluorocarbon, while leaving behind uncontaminated continuous Au lines showing bulk electrical conductivity. This results in going through 12 orders of magnitude in the dc resistivity<sup>76</sup> as the film in the laser treated area goes from below to above the onset of percolation. The growth and aggregation of the sputtered Au atoms into larger and larger nanoparticles within this chemically inert dielectric polymer matrix resulted from an Ostwald Ripeninglike process which was found to be greatly expedited above the glass transition temperature of the polymer. The glass transition temperature of the polymer could be manipulated to some degree by controlling the degree of cross linking within the plasma environment.

The spatial resolution of the resultant Au lines was limited by the wavelength of the Eximer laser. Using highly focused scanning electron beams instead as the intense heat sources were shown to reduce this limitation but require operating in a vacuum which lost the important advantage from an applied point of view of being able to work in air afforded by the use of the laser approach. These studies also

gave us an opportunity to test the degree to which Effective Medium Theories allowed us to predict a variety of physical properties of this class of granular materials above and below the onset of percolation.

Time passes. Our original motivation in 1958 was to learn how to generate a variety of materials in thin film form and learn how to control their microstructure, composition, and resultant physical properties, especially magnetic properties in line with IBM San Jose's overall interest in magnetic storage.<sup>11,12,84</sup> The concept of "a thin film" in those early days in the context of any viable magnetic application was of the order of 100 nm thick.

By the 80s, as the active films within more and more complex film assemblies became thinner and surface and interface phenomena played a more important role, our interests had evolved into trying to understand how magnetic surface phenomena differ from bulk magnetic phenomena using *in situ* diagnostic probes such as spin polarized electron spectroscopies versus optical Kerr magneto optics.<sup>85,86</sup> Also of constant interest were interfacial magnetic exchange coupling processes in a variety of magnetic thin film assemblies<sup>87-92</sup> prepared by ion beam sputtered thin films in UHV. Controlled structural modifications by ion beam bombardment of the growing sputtered thin films in a UHV dual ion beam system and structural and compositional *in situ* characterization by Auger and LEED and magnetic characterization by spin polarized electron spectroscopies and Kerr magneto optics were of special interest.<sup>93</sup>

In the early 90s, our interests had also shifted to the study of magnetic two-dimensional ultrathin films, i.e., submonolayer patches. To avoid serious obscuring of the primary magnetic properties by the phenomenon of superparamagnetism, one typically has to have the layers in patches exceeding 100 atomic distances.<sup>94-96</sup> Ultrathin magnetic films coupled through nonmagnetic spacer-layers to a 3D bulk magnetic ferromagnet make possible the engineering of quasi2D-ferromagnets. The magnetization of the overlayer film can be measured separately from that of the bulk ferromagnet by virtue of the small probing depth of spin polarized electron beam techniques.

Nowadays, people are using spin polarized Scanning Tunneling Microscopy to study a variety of magnetic phenomena of single magnetic atoms interacting with one another and with nonmagnetic neighbors in the context of potential future storage concepts. A scanning tunneling microscope when adapted to cryogenic temperatures and high magnetic fields can assemble and probe spin chains, logic gates, and other configurations of magnetic atoms. So, for example, a relatively recent study answered the question of "how many atoms does it take to reliably store one bit of magnetic information," i.e., how small can you make a magnetic structure and does it still act as a classic magnet for data storage. Assembling the structure with one atom at a time with an STM showed the number to be 12 atoms for iron. In structures with fewer magnetic atoms, quantum switching effects will dominate. Above 12, there is no quantum switching. For a recent overview of this general area, see Ref. 97.

Clearly, Harold Winters's readiness and ability to interact effectively throughout his 30-year career in our group with applied as well as more basic science oriented colleagues allowed him to make very significant contributions in both applied and basic research areas including surface science issues in projects outside of his own particular activities. Besides all this, Harold was also a real gentleman and will be sorely missed by all of us.

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