The potential of highly charged ions: possible future applications

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Abstract. This paper mirrors and provides references to an invited review talk delivered by the first author at the 13th International Conference on the Physics of Highly Charged Ions. It briefly updates and extends an earlier review (J. D. Gillaspy, 2001 J. Phys. B: At. Mol. Opt. Phys. 34, R93-R130).

1. Introduction
The word "potential" in the title of this paper has two meanings. The first is given by Webster's dictionary as "existing in possibility: capable of development into actuality". This meaning hints at the fact that there are applications for highly charged ions (HCIs) that are "not yet ready for prime time" but may become so in the not-too-distant future. Of course, there are applications for HCIs that are well known and well-established, such as in the area of plasma diagnostics [1]. Examples of the latter can be found in x-ray astronomy [2], solar physics [3], and fusion energy plasmas [4].

Then there is the physical meaning of the word potential, as in "potential energy". The electron binding energy of the hydrogen-like uranium ion, for example, is on the order of 100 keV – a tremendous amount of potential energy for a single ion to carry. In fact, if one could go beyond uranium by less than a factor of two (Z = 173), one would exceed a fundamental limit – the point at which the vacuum becomes unstable in the presence of bare ions and real positron-electron pairs spontaneously appear and fill the empty core levels [5]. The potential of highly charged ions is quite literally huge.

In this paper, the focus is on speculative, but potentially far reaching, applications in two areas: microelectronics and biomedicine.

2. Microelectronics
The electronics industry represents a market of over $100 billion ($100 milliard) worldwide. A key technology in this industry is microlithography, driven by Moore's Law, which dictates that the number of transistors/chip will double every 1.5 years. Today, transistors are so small that they cost less than a drop of bottled water to manufacture, and they are being produced at an average rate that exceeds that at which raindrops are hitting the surface of the earth [6]. Indeed, microelectronic devices are pervasive in modern society, and they impact the lives of us all.

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The potential application of HCIs in the area of microelectronics falls into two categories: (1) the use of the HCIs directly to cause an intense surface excitation and possible rearrangement of atoms and (2) the use of HCIs to generate high energy photons which are then used to modify materials. Both of these are discussed below.

What is it that makes HCIs fundamentally different and potentially valuable for direct surface modification? Conventional particles (photons, electrons, or singly-charged ions) are all frequently used to modify surfaces, but virtually never does a single one of them possess enough energy to have much of an effect. Hence, many particles must be delivered to any given region of a surface (“pixel”) that one wants to modify. This requires precise control in the placement of the particles on a length scale that is much smaller than the pixel size. HCIs, on the other hand, carry enough potential energy that a single one of them is sufficient to modify the surface noticeably and with essentially 100% probability. Furthermore, this energy is confined in a natural sub-nanoscale atomic package that cannot be varied even if one tried to do so – it is fixed by the laws of quantum mechanics. This contrasts with a conventional ion beam lithography system, for example, in which many ions must be delivered to a pixel with high accuracy (both in position, and in the number of particles). Additionally, a much lower flux of HCIs is required, since each one is so powerful. In contrast with accelerator-based fast ion microbeams, the potential energy in HCIs allows one to use slow ions that are much easier to create, and in some ways easier to control.

As silicon is a key material in the microelectronics industry, it is natural to focus on this material when considering applications. H.-P. Cheng has calculated [7] the response of silicon to the sort of localized charge buildup that might occur when an HCI neutralizes itself upon impact. The simulation predicts shock wave formation and the ejection of many ions and even more neutral particles, resulting in the formation of a nano-scale crater. Early work at NIST by Minniti used a Scanning Tunneling Microscope to search for such craters after impact by Xe44+. Although craters were detected, the experiments were not definitive, and remained unreported in the literature. Just last year, Ohtani’s group published the first report of silicon cratering which claimed to show a clear charge state dependence [8]. The response of many other surfaces to HCIs has been studied as well. Examples from the NIST Electron Beam Ion Trap (EBIT) Team include CR-39, mica, PMMA, graphite, L-valine, alkanethiol, tungsten, gold, ruthenium, and aluminum oxide [9].

Of particular interest because of their extremely regular geometric shapes, and because they occur on metals, are the self-assembled hexagonal structures we observed on Au(111) after Xe44+ bombardment [10]. It has been suggested that these features might be useful for nanoindentification/nanomarking, for example in anticounterfeiting measures by the drug industry [11]. It is not yet known for sure whether these structures are created by the ion potential energy, kinetic energy, or (as is more typical) some combination of both, although very recent evidence suggests that it may be primarily the kinetic energy [12]. For many applications, however, the distinction may be irrelevant.

From the work of Hayderer et al [13] in the Vienna group of Aumayr and the Berlin group of Stolterfoht, we know that both the ion potential and kinetic energy contribute to the HCI response of aluminum oxide and magnesium oxide. Realizing that these materials are frequently used to make magnetic tunnel junctions (devices with major potential applications in nonvolatile memory, field sensors, “spin transistors”, high frequency oscillators such as spin-torque nano-oscillators, etc.), Andrew Perrella has proposed to use HCIs to tune the electrical properties of thin film oxides in the fabrication of these tunnel junctions. We call this the technique of "Highly Charged Ion Modified Oxides" (HCIMO).

Early studies we have done in collaboration with Perrella and colleagues at Cornell using ballistic electron emission microscopy to examine HCI bombarded thin films suggested that the HCIMO technique was indeed feasible. The NIST EBIT ion-surface facility has now been upgraded by J. Pomeroy, A. Perrella, and H. Grube to allow the fabrication of analogs of tunnel junction devices with oxide layers as thin as approximately 1 nm. To date, we have fabricated over 1,000 such devices, and have demonstrated that the conductance through the oxide can indeed be systematically modified by
applying varying doses of Xe$^{44+}$ ions, at energies of 5 keV per ion charge to 8 keV per ion charge (220–350 keV) [12]. In this device fabrication scheme, we demonstrate that nanoscale effects can be utilized without the need for precise ion positioning.

Another class of applications would be opened up if HCIs could be precisely positioned, however. This has been achieved at the 10 micrometer scale with both fast and slow ions. At GSI, a pointillist painting of Helmholtz was generated on a "canvas" much smaller than the head of a pin, with each point being created by the impact of an individual fast ion (see the figure from Fischer and Metzger shown in [1]). At LLNL, HCIs from an EBIT were focused to 20 micrometers and used to image grid lines thinner than the width of a human hair [14]. More recently, as reported elsewhere in this volume, beams of slow HCIs with widths less than 1 micrometer have been produced inside microcapillaries [15]. These advances open up the possibility of delivering localized doses of quantized (atomic line) x-ray radiation to specific parts of an individual cell, as the ions neutralize on surfaces at the end of the microcapillary. On even shorter length scales, Schenkel and Schneider have been using the Berkeley EBIT facility in collaboration with colleagues at Berkeley, Japan, and Germany to direct HCIs through nanoscale apertures [16] and enable single ion placement with nano-scale accuracy by integration with a scanning probe microscope for applications in quantum computing [17].

There have been reports in the literature from Japan that the high energy density generated by the neutralization of HCIs on carbon surfaces leads to the production of diamond nanocrystals [18]. Supporting evidence for this conclusion was recently presented by Briand's group in France [19]. Earlier studies with scanning probe microscopes over a wide range of charge states have demonstrated that the potential energy in a single HCI contributes to the generation of a nanoscale dot at each ion impact site [20-23].

Luminescent silicon holds promise for applications at the interface between conventional electronics and optical communications. In the late 1990’s, one of us (Gillaspy) proposed that the high nanoscale current density generated when a single HCI neutralizes on a surface might permanently transform silicon into a luminescent form, in analogy to the known process that occurs on a macroscopic scale in spark processed silicon [24]. The LLNL group published evidence for the realization of this idea in 2001 [25], and provided spectroscopic evidence for quantum confinement and the formation of ensembles of silicon nanocrystals. An independent followup experiment at NIST sought to reproduce and expand on this work by using a continuous wave laser-scanning confocal microscope to directly image individual silicon nanocrystals. Although the NIST experiment could detect single fluorescent molecules, it failed to detect any photoluminescence from HCI-processed silicon, and put stringent upper bounds on the effective cross sections under the conditions studied at NIST [26]. Various important differences between the LLNL experiment and the NIST experiment are outlined in the second report [26]. Given the potential importance of HCI-processed silicon, additional experiments would be welcome under a wider variety of conditions. The potential impact of this work is enhanced by recent reports demonstrating the utility of semiconductor nanocrystals for improving the efficiency of solar cells [27].

Presently, highly charged ions are slated to be used by major electronics manufacturers in the so-called "Next Generation Lithography" tools that will be used to mass produce microelectronic circuits in the future. Industry roadmaps currently have these tools slated for introduction into commercial production of nanoscale feature sizes (the 32 nm node) within a few years from now. The successful operation of the ETS alpha-tool in 2001 [28], based on 13.5 nm extreme ultraviolet (EUV) light emitted from highly charged xenon ions, paved the way for more recent developments. Zeiss has demonstrated as early as 2003 the production of lines as narrow as 35 nm in their EUV lithography systems. The key remaining question is whether the overall production method can be sufficiently optimized to allow an acceptable profit margin within consumer price demands.

For several years, the International SEMATCH consortium had listed the power output of the highly charged ion light source as the #1 item on a list of critical concerns. This topic has thus been one of the highest priority items for research and development in the industry. After a major effort at various places around the world, large improvements in xenon light output have been achieved, and
even further improvements have been made by switching from xenon to highly charged tin plasmas. Although more work remains to be done, last year the light source problem was removed from the numbered list of industry's top concerns and EUV lithography sources based on highly charged ions moved from a concept to a reality [29]. Earlier this year, production of 800 watts into a hemisphere of solid angle was reported [30].

The issue of damage to sensitive lithography mirror optics and the electrodes by particles and photons emitted from the EUV source plasma is now a primary concern. We alerted the industry to the fact that the potential energy stored in the highly charged ions might make this damage more severe, a possibility that had not been considered by the microelectronics community previously.

3. Biomedicine
The advantages of using fast ions in cancer therapy are so evident that dedicated clinical therapy installations for proton therapy have been installed or are being constructed at a variety of locations around the world, including a recent one at the Massachusetts General Hospital and the M. D. Anderson Cancer Center in Texas. There is strong evidence that more highly charged (heavier) ions such as carbon can provide even better treatment outcomes, and dedicated treatment facilities for this extension are also under construction or in operation around the world [31]. All of these installations require large expensive devices to generate ions with sufficient kinetic energy to be able to penetrate deep into the body. Size and cost issues have limited the availability and broader acceptance of this form of therapy.

Slow highly charged ions can be produced much more cost effectively, and with a much smaller device. They have recently been proposed for use in both diagnostic imaging and an alternative form of cancer therapy based on the use of monoenergetic x-rays. These are discussed separately in the following two paragraphs.

Marrs [14, 32] has proposed to use an EBIT to generate a point source of nearly monoenergetic x-rays by neutralizing a beam of highly charged ions on the back side of an x-ray window. The principle is illustrated, for example, in the x-ray data we presented for the case of H-like Ar [33]. This can be extended to higher x-ray energies by using higher-Z elements where the x-ray yield approaches 100% (or even 200%, in the case of a double K-shell vacancy, as recently demonstrated for the case of I53+ from experiments done in the Ohtani group [34]). The value of using monoenergetic x-rays for mammography, for example, has been demonstrated in a study in which trained clinicians were able to correctly identify small breast tumors up to 93% of the time when monoenergetic x-rays are used, while that number dropped to 70–87% when conventional broadband x-rays were used [35]. Besides this conceptually simple extension of conventional diagnostic imaging, other more novel methods, such as phase-contrast imaging, may benefit from the availability of a practical point source of monoenergetic x-rays.

Mendenhall has proposed to go further and use an HCI-based x-ray scheme for resonant combination cancer therapy [36]. Behind this is an old idea that monoenergetic x-rays with an energy tuned to match the peak of an absorption edge of a heavy element loaded into the proximity of cancer cells can be used to preferentially destroy the cancer. In light of the recently discovered "bystander effect" it is now clear that it is not necessary in principle to target the cell nucleus of every cancer cell [37]. Biston and colleagues [38] have published a recent review of data on the survival of rats with glioma treated using monoenergetic radiation, showing spectacular success. In this work, a synchrotron was used to generate x-rays matched to the platinum in drugs that are already approved for use in the treatment of cancer in humans. The adoption of this scheme for widespread use has been hampered by lack of availability of small affordable sources of properly tuned monoenergetic x-rays. In principle, by using ions up to H-like uranium, an EBIT can be used to produce x-rays with energies up to 100 keV, sufficient to penetrate moderately deeply into the human body. Although conventional radiotherapy is done with even more penetrating x-rays produced by electrons with energies in excess of 1 MeV, the mechanism is bremsstrahlung, so the number of useful x-rays at these very high beam energies approaches zero, and the broad continuum of x-rays peaks at substantially lower energy (a
factor of 6 lower, in some clinical machines, for example [39]). Thus the energy difference between an HCl-generated source and a modern clinical therapy device is not as large as it first seems.

The continuous ion flux obtainable from an EBIT is a key factor in limiting the practicality of the biomedical uses of slow HCIs discussed above. In 1996, we increased the achieved ion flux record by several orders of magnitude, to 3 million Xe$^{4+}$ ions/second [40], a benchmark that remains today for EBIT devices. Mendenhall has estimated that another 3 to 4 orders of magnitude and a simultaneous increase in the ion charge state will be required to produce Gray (100 rad) levels of dose in tissue on a practical time scale of minutes. Marrs has proposed a method to increase the EBIT brightness by 4 orders of magnitude [41], partly by increasing the length of the EBIT to values closer to that of an EBIS (electron beam ion source). Donets has proposed new schemes to increase the ion flux from an EBIS by 2 to 3 orders of magnitude [42]. One of the most straightforward ways of increasing the EBIT or EBIS flux is to increase the electron current (typically now 0.15 A for EBIT). Recently, Pikin and colleagues have demonstrated a 10 A EBIS that can produce a time averaged flux of $5 \times 10^9$ Au$^{32+}$ ion per second [43]. It thus seems that there are a number of paths available to reach the required ion flux levels.

4. Conclusion
In closing, we may ask the question: are we on the verge of seeing highly charged ions emerge as an important new tool that impacts the everyday lives of millions of people? According to the current plans of the international semiconductor industry, the answer is yes – within a few years we will be able to go to a local electronics store, purchase a computer, and say "this was made using highly charged ions". Much work remains to be done to make this a reality, however. In the meantime, a variety of other more speculative possibilities are being explored by institutions around the world, and we can only look forward to hearing about the progress along those lines at the next International Conference on Highly Charged Ions, in two years.

Acknowledgements
We acknowledge past support from International SEMATECH, the U.S. Department of Energy Office of Fusion Energy Sciences, and the National Aeronautics and Space Administration.

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