**SHORT COMMUNICATION**

**Direct Generation of Ion Beam Images with a Two-Dimensional Charge Injection Device**

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The use of a two-dimensional charge injection device (CID) to directly image the spatial profile of impinging positively charged ions is described. By this approach, no prior conversion from an ion beam to a photon image is required. Because of the positive response of the device to plasma photons, ions that emanated from the radiofrequency glow discharge source were diverted around a photon stop and focused onto the CID. The resultant ion images were digitized via an external image processor and corrected for dark current contributions. Two-dimensional ion images and single pixel line profiles are presented. (J Am Soc Mass Spectrom 1995, 6, 140–147)

Glow discharge (GD) devices have gained popularity recently in direct solids elemental analysis by atomic emission, atomic absorption, and mass spectrometries [1–3]. Particular growth has occurred in the area of mass spectrometry as GD sources have been successfully interlaced with a number of mass analyzer configurations, which include linear quadrupoles, quadrupole ion traps, magnetic sectors [4–6], and Fourier transform ion cyclotron resonance mass spectrometers (FT-ICR-MS) [7–9]. Glow discharge mass spectrometry (GDMS) also has grown in the types of sources employed. Radiofrequency-powered glow discharge (rf-GD) sources eliminate the requirement that samples be electrically conductive [10]. Sample types amenable to this technique include both conductive and nonconductive materials such as thin film systems, complex ceramic matrices, soils, and simulated defense waste glasses [10–14].

To take advantage of both the wide range of sample types amenable to rf glow discharge ionization and the mass resolving properties of FT-ICR-MS, an rf-GD/FT-ICR-MS system was tested at Oak Ridge National Laboratory [14]. The studies confirmed that ions produced in the rf-GD could be transmitted efficiently through the fringing fields of a 3-T magnet and into the ion cyclotron resonance (ICR) cell without supplemental electrostatic focusing. Based on those findings, a dedicated rf-GD/FT-ICR-MS system was constructed at the Savannah River Technology Center. The system and resultant ion trajectories have been modeled by using SIMION PC/PS2 version 4.0 [15, 16]. These trajectory studies suggested that once ions with relatively small angular divergences (< 5°) were transported through the sampling cone to the entrance boundary of the magnetic field, they were refocused by the converging magnetic field lines and funneled into the entrance of the ICR cell. Two-dimensional (2-D) images of the ion beam throughout the flight path would provide spatial information that would aid in better understanding ion transport to the ICR cell. Because no ion imaging devices were immediately available, a study was undertaken to determine whether or not charge injection devices (CID) could be employed in ion imaging applications.

Presented here are results of the initial feasibility analysis of the use of a CID as a direct ion detector for applications in mass spectrometry. In this study, ions produced in an rf-GD source were focused onto the active surface of a 512 × 512 pixel charge injection device wherein an electrical charge was registered in the same manner as photon signals. Advantageous features of the system are the direct generation of spatially segregated signals and the ability to perform...
background (dark current) subtraction on a pixel-by-pixel basis. The results of this preliminary study indicate that CIDs appear to be well suited for direct ion detection and real-time ion beam diagnostics.

**Background**

Since the advent of channel electron multipliers (channeltrons) in the early 1960s [15], ion detection has been performed almost exclusively by these systems [16]. Despite their advantageous characteristics, ion-electron multipliers do not provide the spatial selectivity required in dispersive, sector-based mass spectrometers. Historically, simultaneous mass detection was accomplished by the use of a photographic plate placed in the focal plane of the spectrometer [17, 18]. This approach has been replaced, in part, by the combination of a microchannel plate (MCP) and a phosphorescent screen coupled to different photosensitive array detectors, which include linear photodiode arrays [16, 19–23], vidicon cameras [20, 24, 25], and charge-transfer devices [26–31]. This mode of detection involves the conversion of the ions to electrons in a honeycomb-like microchannel plate (electron gains of approximately 10^6 are common in dual-MCP Chevron-based assemblies [32]), acceleration of the electrons to a phosphorescent screen for conversion to photons, and finally the spatially resolved detection of the photons imaged on the detector.

Most integrating electrical encoding array detectors exhibit charge blooming, that is, the spilling of photogenerated charge from one channel into neighboring channels as the charge capacity of the element is exceeded. This process results in lowering of the true mass resolution of the spectrometer and increases the probability of quantitative errors. Mass resolution in multistage detector systems is limited by the MCP channel-to-channel spacing and may be decreased by cross talk (signal translation) between adjacent channels. For most MCP-based detector systems, a decrease in sensitivity occurs at the various component interfaces [16]. Fiber-optic couplers have been used to reduce these electron–photon losses. Scattering at these interfaces (i.e., MCP–phosphor, phosphor–fiber-optic, fiber-optic–detector) causes broad, low intensity tails of the detected peaks that results in degradation of resolution [16]. Additionally, this combination has been shown in optical spectroscopy to suffer from 2-D light diffraction which results in spurious signals [33].

Charge injection device (CID) arrays are a class of CTDs that have been utilized for a wide range of applications in analytical spectroscopy, most extensively with electrothermal, spark, and plasma source atomic emission and atomic absorption systems [34–38]. These systems also have been utilized for stellar system imaging [39–41]. For a more complete description of charge injection devices, the reader is referred to review articles by Denton and co-workers [28, 29]. Perhaps the most attractive feature of CIDs is their inherent resistance to blooming, because the charge remains inside the confines of each pixel for sensing, unlike charge coupled devices (CCDs) wherein the charge must be shifted to the periphery of the array for sensing. Once the capacity of the CID potential well has been exceeded, the additional charge diffuses into the substrate and is neutralized rather than being transferred across the array. [Beyond this level of charge (signal), quantification is not possible because that detector element is effectively saturated.] Because the charge is detected at each pixel, readout is nondestructive, which allows for extended integration and real-time signal level monitoring. Additionally, CIDs may be operated in the random access integration (RAI) mode, which allows for separate pixels or groups of pixels to be addressed without perturbation of remaining pixel functions [34].

In terms of direct charged particle detection, charge transfer devices offer a number of strengths, which include high sensitivity and spatial resolving capabilities, that are inherent to the design of the devices. Electrons have been detected without prior conversion to photons by using several different types of solid state detectors. Martin et al. [42] employed a "wedge-and-strip" anode configuration as a detector for electrons exiting a dual MCP configuration. For this detector, only three or four discrete electrodes were employed, which yielded a resolution of approximately 0.4% of the image field size. Germer et al. [43] used a CCD for detection of electrons photomitted by laser ablation of a Cu(III) surface. The electrons were allowed to drift through a field-free region in a time-of-flight system, then were accelerated, focused, and deflected onto the surface of a CCD at which point the electrons had kinetic energies of 5 keV. Most recently, Birkinshaw and co-workers [44, 45] described a high resolution silicon-based discrete array for electron detection. The detector array contained 384 detectors and exhibited a resolution of 25 μm.

The application of charge injection devices for direct particle detection has been limited. Downing et al. [46] employed a CID as a position sensitive radiation detector for imaging of neutrons and α-particles with kinetic energies in the megar electron volt range. The system also was shown to be a high resolution charged particle imaging device that could be operated in a variety of data collection modes. No work has been found in the literature, however, that describes the use of CIDs for low energy positive or negative particle detection.

The work of Kane et al. [47] is pertinent to this study because they recently have imaged ions in the 10–100-eV range, which encompasses the energy range of glow discharge-generated ions. Ion imaging was accomplished by assessing sputter-damaged films of α-terminated polar head groups of self-assembled alkanethiols. Ions bombarded the surface of the monolayer film assembled on a gold substrate and induced loss of the polar α-terminal groups via ion–surface
collisions. Following exposure to the ion beam, the film plates were removed from the vacuum environment and water vapor was condensed onto the surface. The sputtered region was analyzed visually through a water droplet pattern that resulted from the disrupted polar group distribution.

The direct imaging approach described here utilizes a charge injection device that offers potential advantages over other ion imaging and detection techniques. First, ions do not have to be converted to photons prior to detection. Second, resolution is enhanced with CID detection owing to the resistance of the device to charge blooming. Third, the direct detection method allows the ion beam spatial integrity to be maintained. Finally, this technique allows for real-time monitoring of the ion beam that may offer significant utility for analytical spectroscopy. One admitted shortcoming of this technique, however, is the reduction of sensitivity owing to the elimination of signal amplification in the conversion of ions to electrons via MCPs.

**Experimental**

The glow discharge source used in this work has been described in detail by Duckworth and Marcus [48]. The source was employed without modification and was placed within the vacuum housing of a laboratory-built double quadrupole mass spectrometer. For these experiments, the quadrupole assembly was removed and the CID camera assembly was mounted in the normal position of the skimmer cone–differential pumping orifice. Because charge injection devices are responsive to both charged particles and photons, use of the rf-GD source introduced some difficulties to this feasibility study. Specifically, removal of the photons that emanate through the ion exit orifice with the charged particles was a primary consideration. (It is important to note that this is not a concern for ion sources typically applied in organic mass spectrometry.) A Bessel box assembly was proposed to reduce the photon flux and was modeled via SIMION PC/PS2 version 4.0 [49].

Figure 1 shows simulated trajectories of $^{63}$Cu ions being transmitted through the assembly. In this simulation, optimum ion transmission occurred with the photon stop grounded and the isolated walls held at +26 V. Based on the modeling results, a Bessel box-type ion lens was fabricated and placed in front of the imaging system. Figure 2 illustrates the experimental setup employed to reduce the photon component of the signal. In this arrangement, ions were passed around the 1.3-cm-diameter metal disk (photon stop) and partially refocused through a grounded back orifice plate onto the surface of the detector. Obviously, use of the Bessel box assembly effectively prohibits the intended application of use of the CID to monitor the rf-GD ion beam, unperturbed, in the FT-ICR-MS ion transport modeling.

The glow discharge was operated at a pressure of 0.20 torr of argon discharge gas with 20 W of forward power applied to a stock copper pin, which served as the cathode. Studies of the relative ion intensities registered on the CID suggested that an increase in the ion kinetic energy (IKE) led to an increased imaging efficiency. The IKE was altered by changing the potential applied to the electrically isolated sampling cone, with the images presented here taken at the optimum cone potential.

The charge injection device (CIDTEC CID 2250, CID Technologies, Liverpool, NY) employed in this work is a two-dimensional matrix of 512 vertical and 512 horizontal active pixels with a 15-×15-μm format that provides an image sensing area of 7.68 × 7.68 mm. The 2.5-μm charge accumulating electrodes are positioned atop the silicon layer between contiguous pixels; thus, the exposed center-to-center distance is 12.5 μm. The typical background noise is 5 nA (rms) and the subtractable fixed pattern noise is 25 nA (rms) with a
saturation current of 900–1000 nA at 10 MHz (element rate clock) (D. M. Carta, CIDTEC, Liverpool, NY, personal communication). The CID was progressively scanned at a frame rate of 30 Hz with noninterlaced readout at a rate of 62.5 μs per line. The camera was operated in the “inject inhibit” mode to allow for extended integration of the ion image. This feature inhibits the single frame destructive read process and allows charge to build on the sensor for a specified number of frames. For this study, charge was accumulated for 100 frames without suspension of scanning during integration for a total integration time of 3.2 s. Resolution degradation as a function of increased integration time was not observed, which confirms that charge blooming does not occur in this detector system.

The CID 2250 is fabricated with the active silicon wafer mounted in direct contact with the readout electronics. This configuration results in conductive heating of the silicon and thermally generated charge production. The dark current has been shown to double for approximately every 8 °C increase in temperature ranging from 0.003 nA/cm² at −12 °C to 1.8 nA/cm² at +50 °C (D. M. Carta, CIDTEC, Liverpool, NY, personal communication). The device was not cooled during this work because of physical constraints of the vacuum housing; therefore, thermal noise rapidly increased as a function of time. Further utilization of this technique will, therefore, require development of a cooling system such that the signal-to-noise characteristics may be improved. To correct for the thermal contribution to the signal, a commercial image processor (EPIX 4MEGVIDEO, EPIX, Inc., Northbrook, IL) was integrated into the imaging scheme to allow for signal digitization and deconvolution. Figure 3 illustrates the basic signal processing pathway. The camera is connected to the camera control unit (CCU), which is powered by the “easy integrator” (ICM7000) module. ICM7000 operations are controlled via a hand-held terminal. The video output of the CCU is input to the 4MEGVIDEO board and the final 4MEGVIDEO signal is dumped to 1 of 16 available memory buffers and to the monitor for visual display. Images that are stored in memory buffers may be manipulated through image processing routines such as averaging and subtraction functions and pixel-by-pixel display for comparative operations.

For this study, images were collected in sets of four that included a background image. Following data collection, the camera was turned off for 15-min intervals to allow for the active surface to cool. Without sufficient cooldown, pixel saturation due to thermally
Figure 3. Block diagram of the image processing system.

Figure 4. Two-dimensional images of ions extracted from a radio frequency glow discharge source operated under optimum conditions: (a) raw image, (b) background image, and (c) background corrected image.
Figure 5. Single horizontal pixel line \((y = 262)\) image of ions extracted from a radiofrequency glow discharge source: (a) raw signal, (b) background signal, and (c) background corrected signal.
generated charge precluded ion image collection. The three ion images and the associated background were each stored in a separate buffer. The background was subtracted from each image.

**Results and Discussion**

Initial studies were conducted with the walls of the Bessel box biased at +26 V based on the SIMION simulation results, and the photon stop and back plate were grounded. Ions were extracted from the plasma through the sampling cone biased at +12 V (the potential at which the greatest ion transmission was achieved). The image was, however, barely discernible even after background correction. The Bessel box potential was found to have a pronounced effect on the registered image. A study of the measured ion image pixel intensities as a function of Bessel box potentials indicated that a potential of +20 V applied to the walls of the box yielded maximum ion intensities as registered by the CID. The difference in the simulation and experimental wall potentials (6 V) is not considered significant given the loose tolerances allowed in this initial design.

Figure 4a is the two-dimensional ion image captured after 100 integrations of the signal obtained with the optimized conditions as previously described. A Gaussian-like signal superimposed on a broad continuous background is clearly visible in the central portion of the device surface. Figure 4b is the equivalent background contribution measured under the same capture conditions with the plasma extinguished. As can be seen, a large portion of the signal detected in Figure 4a is due to the electronic background that results from detector heating by the support electronics. Figure 4c depicts the resultant ion image obtained after subtraction of the data in Figure 4b from Figure 4a. The image shown in Figure 4c indicates that the background subtraction is quite effective in recovery of the true ion image. Figure 5a, b, and c corresponds to the total signal, background signal, and background corrected signal, respectively, for a horizontal line located in the center of the image (y = 262). The final image shows that the ion beam is symmetrical and approximately 4.5 mm in diameter under the ion optics conditions mentioned previously. These data indicate that the direct detection and imaging of positive ions with a charge injection device for mass spectrometry is indeed feasible.

**Conclusions**

Ions that emanate from a radiofrequency glow discharge have been imaged successfully by using a charge injection device as a detector. It is important to note that the device was applied in a manner analogous to simple optical imaging applications with no modifications to the detector or the electronics. Plasma photon flux was reduced by placement of a Bessel box in the camera line-of-sight; therefore, the resultant image corresponds chiefly to ions that impinge on the CID surface. The findings of this study suggest that the rf glow discharge-generated ions of approximately 30–50-eV induce charge in the epitaxial layer of the CID, although thorough energy studies were not conducted. This system has several attributes: it allows for direct imaging of low energy ions without postacceleration, which causes ion beam distortion, it reduces apparatus complexity by elimination of the need for conversion of ions to photons, and it maintains image spatial profiles owing to the resistance to blooming.

**Acknowledgments**

The authors gratefully acknowledge CID Technologies, Inc. and EPix, Inc. for the use of equipment and for technical support. Project funding was provided by the South Carolina Universities Research and Education Foundation.

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