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Field-Emission Cold-Cathode EI Source for a Microscale Ion Trap Mass Spectrometer

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A cold-cathode electron impact ionization source based on field emission from an array of diamond-coated silicon whiskers is described. The source is coupled to a microscale ion trap mass spectrometer ($r_0 = 0.50$ mm, $z_0 = 0.50$ mm). An electron beam of 250 nA could be obtained through the 0.45-mm diameter opening in the end cap electrode.

Electron impact ionization is a widely used method of generating ions of gas-phase molecular species in analytical mass spectrometry. The source of electrons in laboratory instruments is generally a thermionic cathode, typically a tungsten or tungsten−rhenium filament operated at temperatures of 1000 K or higher.[1] These sources are simple and robust and supply copious quantities of low-energy electrons that can be gated, focused, and accelerated into a beam of high brightness. However, there are also needs currently for miniature instruments that can operate with limited power consumption. In such instruments, the power required to heat a filament might be a substantial fraction of the total electrical demand. The situation is somewhat analogous to the battery requirements of older model portable radio receivers that used vacuum tubes compared to modern receivers using solid-state components. The purpose of this paper is to describe some experiments with a cold-cathode electron source formed from an array of diamond-coated silicon whiskers. A bias voltage applied between the whiskers and a fine-mesh anode caused field emission from the whiskers. The resulting electron beam was coupled to a 1-mm-diameter ion trap to evaluate its performance as an ionization source for atomic and molecular species.

There is a great deal of interest in low-voltage electronic field emission driven by possible applications in flat-panel electronic displays.[2] An addressable array of field emitters could be placed behind a phosphor screen to make a very thin display device. Many of the approaches are based on photolithography and micromachining fabrication to achieve the desired pixel density and electrode separation. Most are in the experimental stage and some are proprietary. A method that is being explored at the Institute of Crystallography, Moscow, is to fabricate arrays of sharpened silicon whiskers that have been coated with vapor-deposited diamond.[3] If an anode or positively biased grid is placed close to the tips of the whiskers, electrons can be extracted from the whiskers. Currents greater than 1 μA/tip have been reported[4] with a threshold external electric field as low as 1.5 V μm^{-1}.[5] The whiskers have been grown in random arrays or with regular spacing with separations from 16 to 100 μm. Several configurations of these whisker arrays are now available commercially for experimentation (Containerless Research Inc., Evanston, IL)

The theoretical basis for electron emission from diamond in general and from diamond-coated whiskers is still controversial. The negative electron affinity of hydrogen-passivated diamond surfaces undoubtedly is important in reducing the threshold field.[6] However, other forms of carbon electrodes such as nanotubes[7,8] and diamond-like carbon[9] also show anomalous emission behavior. Givargizov et al.[10] have proposed a model for the electron emission from their diamond-coated whiskers based on that of Latham and co-workers.[11,12] In this model, electrons tunnel from the highly doped n-type whisker through the layer of diamond that is assumed to be intrinsic until they reach the field-depressed conduction band. Because of the negative electron affinity of diamond, there is no further barrier to emission. Since the conduction band depression due to field penetration is proportional to the external field, the current−voltage dependence for this model would be similar to that for conventional field emission. Other observed effects, however, such as hysteresis and current saturation, are not explained.[10]

EXPERIMENTAL SECTION

The whiskers (Containerless Research, Inc.) used for the electron source were spaced 100 μm apart on a square pattern to form a roughly circular array 2 mm in diameter. They had been grown on a 1-cm-square by 1-mm-thick silicon base. The whiskers

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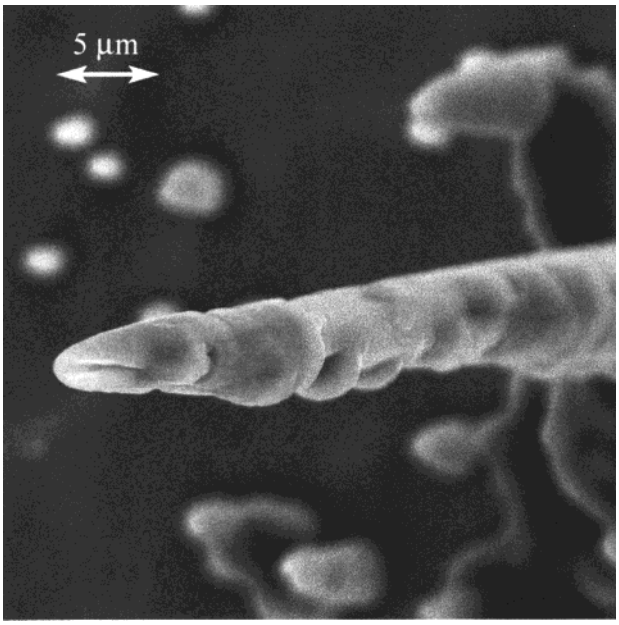

Figure 1. Scanning electron micrograph of a diamond-coated whisker.

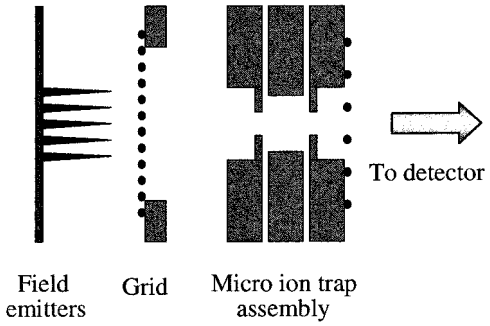

Figure 2. Microscale ion trap mass spectrometer assembly.

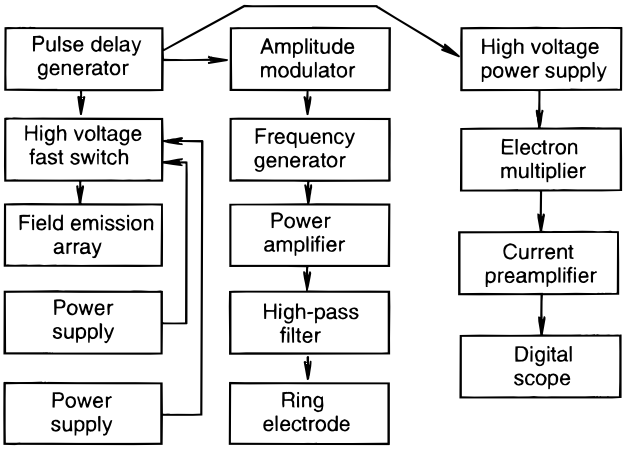

Figure 3. Block diagram of the electronics circuitry.

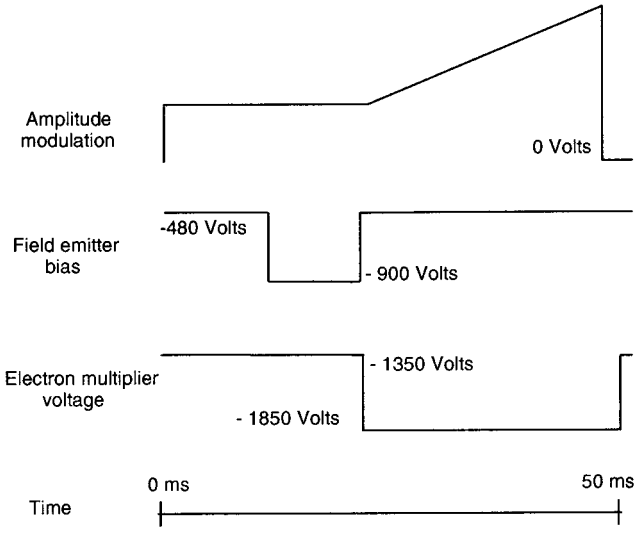

Figure 4. Timing diagram for a typical mass scan.

were approximately 100 μm high and coated on the tips with CVD diamond. A scanning electron microscope image of one of the coated whiskers in the array is shown in Figure 1.

The counter electrode was a nickel screen, 250 wires/in., with 70% transmission. The hole spacing was slightly less than the whisker spacing so there would be a possible convergence of the emission beam. The whisker base was fastened to a stainless steel disk with silver-filled conducting epoxy. The counter electrode was positioned between the whisker plate and the front end cap of the ion trap with appropriate insulating spacers, as shown in Figure 2. The distance between the whisker tips and grid was estimated to be approximately 100 μm.

The ion trap was of cylindrical form with 1.0-mm internal diameter.[13] The ring electrode was 0.90 mm thick and with mica spacers; the separation between the planar end caps was 1.0 mm. An axial hole 0.45 mm in diameter was drilled in each end cap for passage of the sample gas, electrons, and ions. The entire assembly of backing plate, whisker base, grid, trap electrodes, and spacers was screwed to a mounting plate with a channel electron multiplier mounted on the other side, as in Figure 2. A coarse nickel screen, 100 wires/in., 85% transmission, was used to shield the ion trap from the high dc potential of the electron multiplier. The multiplier was a Gallileo 4773G Channeltron with conversion dynode and input screen removed. The ion trap was operated with the two end cap electrodes grounded. The entire assembly was mounted in a six-way, 15-cm Conflat cross, pumped by a turbomolecular pump to a residual pressure of 4×10^{-7} Torr.

The electronic circuitry to operate the ion trap was basically the same as described previously[13] with an additional high-voltage fast switch to control the electron beam. A block diagram is shown in Figure 3.

The timing of the scan function was controlled by a digital delay generator that triggered an amplitude modulation function generator to define the time dependence of the rf voltage. The delay generator also caused a reduction in voltage on the electron multiplier during ionization and the application of a negative bias to the whisker base to produce an ionizing electron beam. The necessary voltages were generated separately by high-voltage dc power supplies. The multiplier supply could be switched between two levels by a TTL pulse, while the whisker bias was generated by two fixed high-voltage supplies and a high-voltage pulse generator. The supplies were switched between two levels rather than to zero to minimize the switching transient-induced noise in the detector current preamplifier. The output from the preamplifier was processed by a digital oscilloscope.

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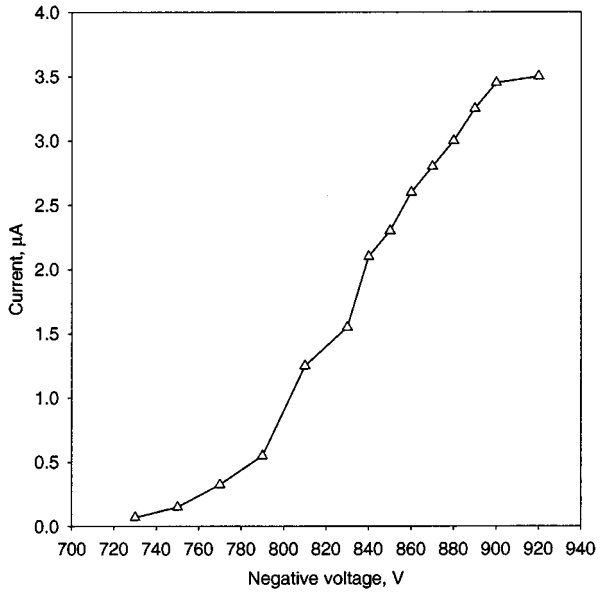

Figure 5. Current−voltage curve for whisker array.

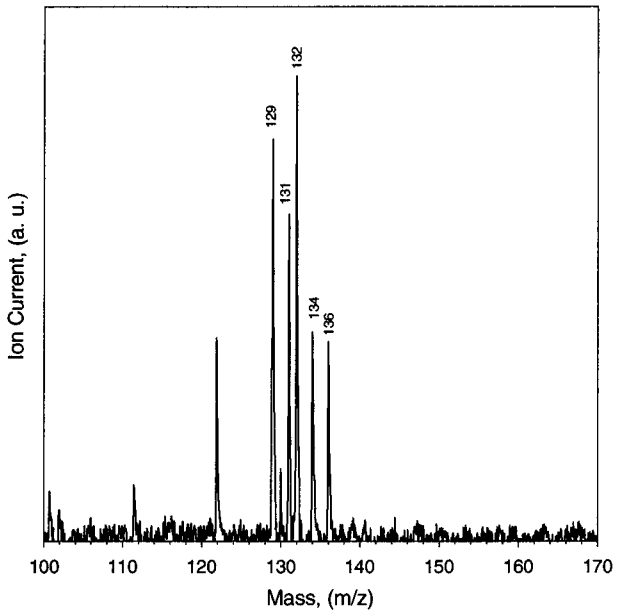

Figure 6. Single-scan mass spectrum of xenon.

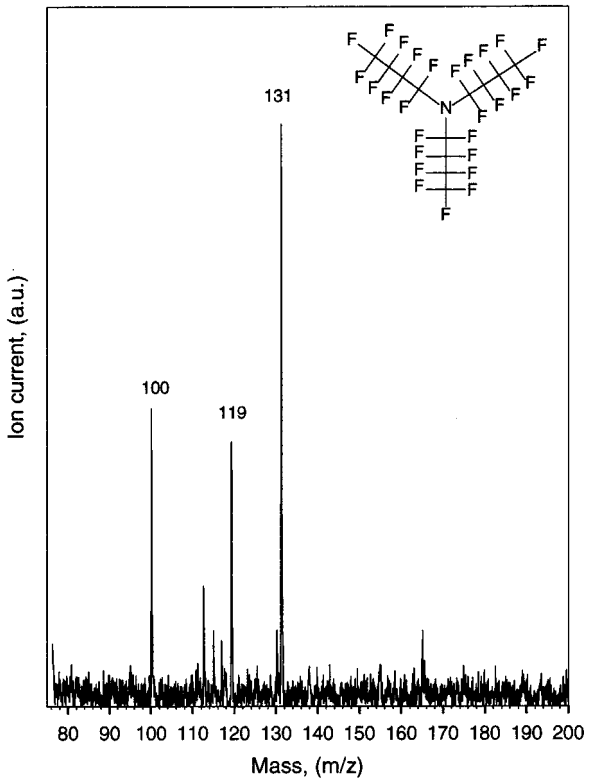

Figure 7. Single-scan, partial mass spectrum of PFTBA.

A timing diagram showing a typical mass spectral scan is given in Figure 4. The output of the amplitude-modulated rf generator was power amplified and fed to the ring electrode through a high-pass filter with dc path to ground to avoid electrode charging. The rf voltage on the ring electrode was typically 55 V_{0p} during the ionization−ion storage portion of the scan and was then ramped from 55 to 195 V_{0p} in 30 ms to eject the ions. The rf frequency was between 4.5 and 6.5 MHz, depending on the desired mass range. The ramp of the amplitude modulation generator was adjusted to compensate for partial saturation of the rf power amplifier at higher amplitudes so that the output voltage ramp was approximately linear with time.

For mass spectrometry, the vacuum chamber was filled with helium buffer gas at a pressure of 10^{-3} Torr. While trap performance (sensitivity) improved as the pressure was increased, the electron multiplier became excessively noisy when the pressure approached 4×10^{-3} Torr. Two samples were studied in this investigation, xenon and perfluorotributylamine (PFTBA), the former an atomic sample with a characteristic isotopic signature and the latter a well-studied molecule whose electron impact ionization fragments are often used for ion trap mass calibration in the 50−650-Da range. The samples were introduced by filling the chamber to a pressure of 10^{-5} Torr of the desired substance before adding the helium buffer gas.

RESULTS AND DISCUSSION

A current vs voltage curve for the whisker array is shown in Figure 5. Current values in the plot were visual averages of the fluctuations observed on the oscilloscope during the 10-ms pulses of the bias voltage. Some hysteresis was observed while the bias voltage was varied. The values in Figure 5 were measured as the bias voltage was reduced from the maximum, saturation level. The current shown was the total current collected by the three ion trap electrodes connected together. The current passing through the hole in the front end cap electrode (collected by the ring, rear end cap, and detector) saturated at 250 nA. The ratio of the two currents was approximately equal to the ratio of the area of the hole in the electrode to the total area of the 2-mm-diameter whisker array.

A single-scan mass spectrum of xenon is shown in Figure 6. For these measurements, the ion trap scan function was repeated periodically and a single sweep of the digital oscilloscope was saved. A mass resolution of approximately 0.2 Da could be obtained in this way. Power rf amplifier jitter in repeated mass scans degraded the mass resolution to approximately 1 Da when several scans were averaged together. The major isotopes of xenon are labeled in the figure. Some other minor peaks appear in the spectrum that are not due to xenon that are attributed to

the escape of trapped xenon ions or to charge exchange with lighter background molecules whose ions would be unstable in the trap. The voltage on the ring electrode had a frequency of 6.5 MHz for these measurements.

A mass spectrum of a molecular species, in this case, PFTBA, is shown in Figure 7. The labeled ions are some of the fragment ions characteristic of this compound. This mass spectrum was acquired with a frequency of 5.5 MHz for the ring electrode voltage. We were able to scan over only a limited range of the fragment ion spectrum of PFTBA.[14] Sensitivity fell off rapidly when the ring voltage was less than 55 V_{0p}, and the upper voltage limit was determined by the output of the power amplifier. The lower and upper m/z values for a single scan based on the mass-selective instability were proportional to these two voltages.[15] The m/z values covered by a spectral scan could be varied by changing the rf frequency so that a total range from approximately 40 to 400 Da could be measured with overlapping scans.

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These results show that it is possible to obtain mass spectra with a cold-cathode source for electron impact ionization. The electron current from the cold-cathode source in the present investigation was 1 order of magnitude smaller than we achieved with a hot filament source and an ion trap of similar dimensions. However, the present source is much more compact, has lower power consumption, and is amenable to microfabrication. Microfabrication techniques should make possible a cold-cathode source with much better control of the emitter to anode separation that can operate with applied voltage of 100 V or less.[2]

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