Search for Fractional-Charge Impurities in Silicon Using Infrared Photoionization and Field Ionization

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A search for unconfined fractional charges in Si based on fractional-charge impurity energy-level predictions of Chaudhuri, Coon, and Derkits [Phys. Rev. Lett. **45**, 1374 (1980)] is described. An upper limit (95% C.L.) of 2.3×10^{-20} fractional charges per atom is obtained using a combination of an infrared photoionization and a field ionization technique. This optoelectronic approach has the advantage of giving an estimate for the concentration of fractional charges, being repeatable and without mechanical techniques. By comparison, drop type experiments detect the presence of fractional charge modulo one unit of fractional charge.

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Although pointlike fractionally charged constituents within hadronic particles have been clearly demonstrated experimentally, searches for free fractional charge in natural materials have not yielded any substantiated positive results [1,2]. The commonly accepted theoretical view is that at least one class of fractional-charge particles (FCP) is absolutely confined in integer-charge bound states. This view has made it appear doubtful that searches for fractional charge will be successful. On the other hand, newly developed theories must be tested and some past searches may have suffered from the elimination of FCP's from samples prior to or during experiments.

This new FCP detection method is based on Chaudhuri, Coon, and Derkits' prediction [3] of the existence of localized states in semiconductors associated with electrons or holes weakly bound to fractional-charge impurities (FCI's), and the integer-charge experimental results [4]. In principle, the spectrum of states of electrons or holes weakly bound to FCI's could provide an experimental signature for fractional charge which is nearly as detailed as the H_2 spectrum. Fractional-charge elements [5], if they exist, would consist of quarks or quarks bound to nuclei [6] surrounded by electrons and would not be neutral.

In analogy with the well-known shallow "donor" impurities in semiconductors in which an electron is weakly bound to a positive ion $D=D^{+}+e^{-}$ the existence of shallow fractional-charge donors has been predicted [3], $D^{-1/3}=D^{+2/3}+e^{-}$, $D^{-2/3}=D^{+1/3}+e^{-}$.

For a hydrogenic system, the binding energy is $(m^*/m_0)[Z/\kappa]^2\times13.6(\mathrm{eV})$. Phosphorus in Si:P is similar to a proton bound to a Si atom giving rise to shallow levels, which can be observed by infrared (IR) spectroscopy [7]. The Z^2 scaling of hydrogenic energy levels has been found to hold true in the effective mass approximation [8], suggesting that impurity levels also scale as the square of the ionic charge, including fractional ionic charge. For $Z<1$ valley-orbit splitting and central cell correction are less important relative to the effective mass approximation as they scale as Z^4 [3].

Shallow levels for integer ions have been observed [4] via a $1s(A_1)$ to $2p^{\pm}$ transition peak [in the photoresponse at 32 μm (38.7 meV)] using this technique. This corresponds to the experimentally observed transition energy (39.2 meV) [7] and the effect of reducing the Coulomb barrier by an electric field. The presence of the field causes the $2p^{\pm}$ state to be above the classical photoionization threshold (see inset in Fig. 3). The integrated effect of $1s(A_1)$-$2p^{\pm}$ photoionization is observed (after an IR exposure) by ground-state $[1s(A_1)]$ field ionization [9]. For a Si nucleus with a bound u ($Z=\frac{2}{3}$) quark (FCI), the $1s(A_1)$ to $2p^{\pm}$ transition energy corresponds to 87.9 μm and the electron binding energy to 78 μm [3].

Sensitivities of 1 FCI/10^{19} nucleons (in 10^{-5} cm^3) were expected [10] in photoelectric spectroscopy techniques. At sufficiently low temperatures, cross sections for the capture of an electron or hole by a charged impurity are large [11,12] and no significant thermal ionization of occupied impurity levels occurs. For shallow impurity levels it is possible to detach a bound electron or hole by applying an electric field. At fields below the classical ionization field, this is predominantly a tunneling process. A low-temperature technique for observing the repetitive cycle of quantum mechanical field ionization (QMFI) of shallow impurities followed by injection of carriers and deionization by carrier capture has been demonstrated [13].

A reverse-bias voltage across a p-i-n structure can establish fields of the order of 1 V/μm in the i region, sufficient to cause QMFI of shallow impurities which can remain ionized or deionized for long periods. The shape of the expected signal is obtained from the QMFI rate $R\propto\exp(-\mathrm{const}\times Z^3/F)$, where Z is the charge of the impurity center after electron detachment and F is the electric field [14]. The strong dependence on the charge suggests a means of producing a signal from FCI's by field detachment of bound electrons producing a small background from a larger population of integer-charge impurities. Deionization is accomplished by carrier capture following injection of carriers from the n or p regions, photoexcitation of carriers across the gap, or excitation of carriers by ionizing radiation.

The charge release of QMFI is seen as a peak on top of a plateau associated with the capacitance of the device [13]. First a forward-biased pulse injects and traps carriers in shallow impurity levels. The diode is then illuminated with an IR beam, and simultaneously a reverse-bias field is applied which sweeps away photoexcited carriers. The field is low enough that QMFI rates are negligible; hence infrared photodetachment depopulates the occupied ground-state levels. After exposure to IR, a fast pulse depopulates the remaining ground-state population. The IR approach probes both the effect of the field on the photodetachment threshold and the excited states through excited-state field ionization.

Our experiment utilizes two 0.92 in. diam Si *p-i-n* diodes with 400 μm thick *i* regions representing the sample and the reference (Fig. 1) which was not exposed to IR. Figure 1 shows the circuit diagram and the wave form used in the experiment. The National Synchrotron Light Source IR4 beam line, which is a pulsed, broad band ($1-10^3$ μm) and of high intensity, was used as the

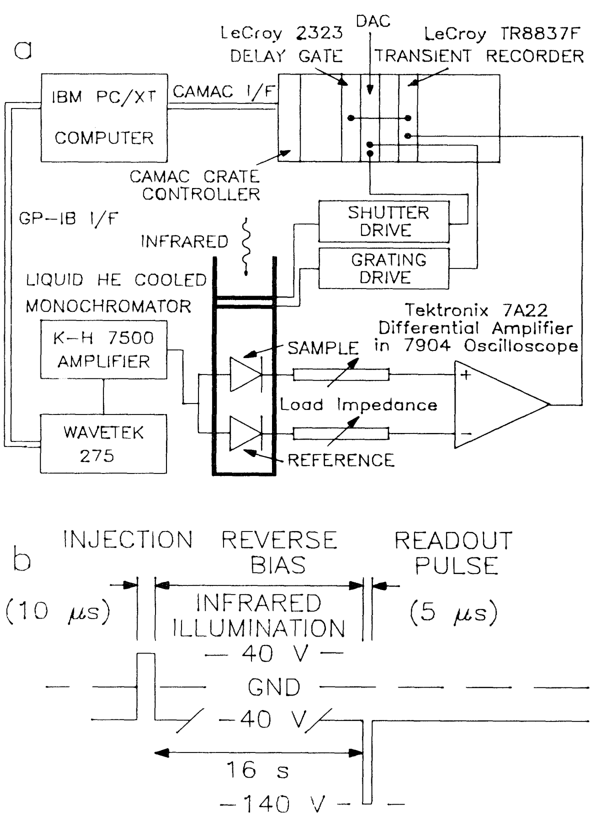

FIG. 1. (a) The electronics used to measure the difference in charge released by the sample diode, which is exposed to IR, and the reference diode, which is not. The data, shown in Fig. 3, are digitizations of the difference amplifier output taken as a function of time after the readout pulse. (b) Input wave form applied to the two diodes.

IR source. To block shorter wavelengths, which can ionize integer charges, three sets of Infrared Laboratories SrF_2/diamond powder 60–200 μm long pass filters were used. Charge was initially injected into the device by a forward-biased pulse (rise and fall time $=8$ μs, plateau $=10$ μs, field $=0.1$ V/μm) deionizing the impurity sites in the *i* region. The diode was then reversed biased (0.1 V/μm) and the *i* region exposed to an IR beam ($\lambda=78$ or 69 μm) for a time interval (16 s), sweeping out only the photoexcited and very shallow carriers (D^-, D_2^-, and $D^{-2/3}$) (Fig. 3). The FCI's (with $Z=\frac{2}{3}$) are excited by $\lambda=78$ μm but not by $\lambda=69$ μm [3]. Readout was accomplished by a large (0.35 V/μm, width $=5$ μs) reverse-bias pulse. The FCI's ($Z=\frac{2}{3}$) would give a signal only if IR with $\lambda=69$ μm releases charge with the readout QMFI pulse into the load capacitor.

Output signals were recorded via a Tektronix 7A22 differential amplifier ($R_i=1$ MΩ and $C_i=47$ pF) in a Tektronix 7904 oscilloscope with a typical voltage gain of 2500. Care was taken to match the impedance of the signal and the reference diodes at the input to the differential amplifier, to account for small differences between the two diodes and the capacitance of the cables. A high degree of nulling permits effective use of the high (10^5) common mode rejection ratio. The bandwidth (30 kHz) of the differential amplifier was set to correspond to the time constant associated with the load capacitance and resistance. In addition, a subtraction is performed between IR-on and IR-off signals associated with the open and closed shuttering of the monochromator, providing another level of cancellation. The output signal was digitized with a LeCroy TR8837F transit recorder sampling at 8 MHz. Reduction of the background at lower wavelengths due to ionization of integer charges was accomplished with a cryogenic monochromator (Fig. 2) and filters operating at $T=2.3$ K (achieved by pumping on liquid He). The Dewar head features vacuum tight mechanical, electrical, and optical feedthroughs which are necessary for extended operation below 4.2 K. The shutter was controlled through a stepper motor connected to the IBM PC/XT through the CAMAC system, used for data acquisition and control of the experiment.

Data sets (each consisting of the mean of 300 waveform cycles) were taken for each wavelength (78 and 69 μm) above and below the photoionization threshold for FCI's with the shutter open (IR on) and closed (IR off). Each data set was filtered of its high frequency (≥ 156 kHz) components. A difference was then obtained for each pair of IR on and off data set. Eight such difference data sets were then averaged. The observed dispersion of these data sets gives us an estimate of the fluctuations due to environmental conditions. They are approximately constant as a function of time, up to 24 μs, where a background from integer-charge impurities begins to influence the data. The magnitude of the systematic effects is represented as an error flag in Fig. 3.

To analyze field ionization dynamics, the following

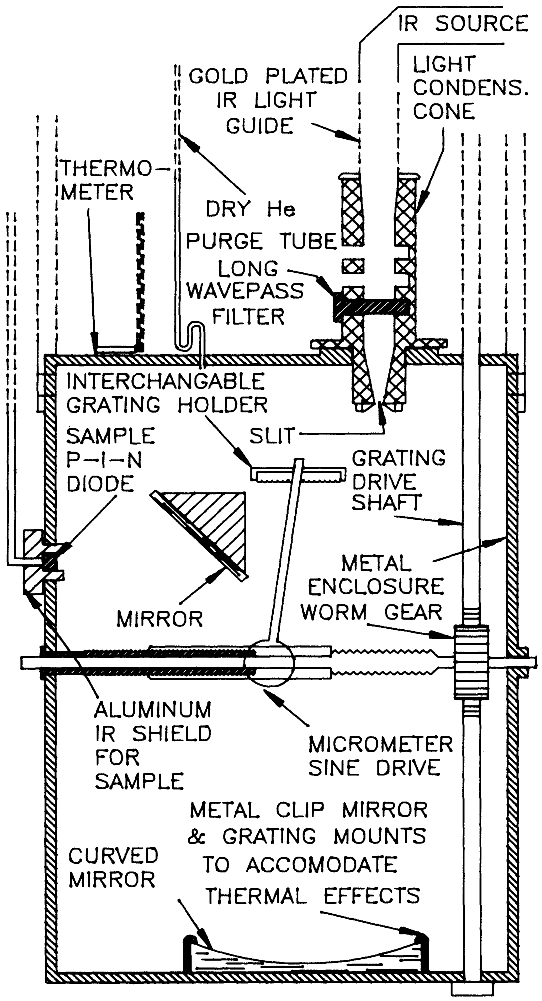

FIG. 2. Cryogenic monochromator with low-temperature long-wave-pass filters.

analysis was performed. The rate of change of the number N of unionized impurities will be given as

$$\frac{dN}{dt} = -RN \,, \tag{1}$$

where R is the QMFI rate mentioned above. Integrating Eq. (1), we have

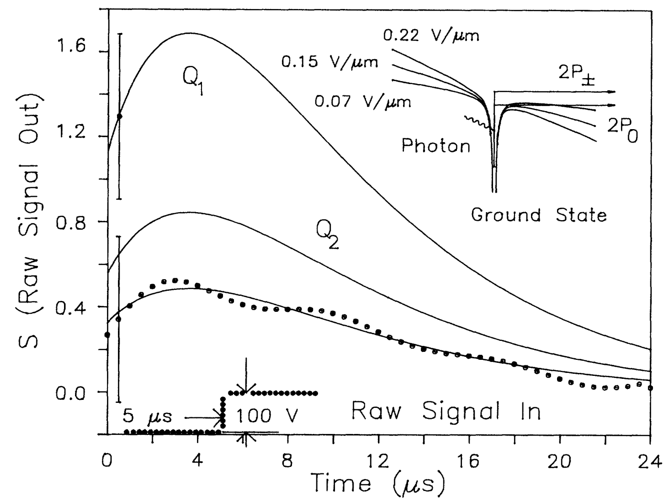

FIG. 3. Experimental data (circles) and fitted function of Eq. (3) (solid line). The error flag indicates the size of the signal fluctuations due to environmental changes. Q_1 and Q_2 denote the expected signal if 400 and 200 FCI's are present. The dark dotted line shows the timing of the negative pulse used to remove the charges. Inset: The electric field enables the impurity electrons to overcome the Coulomb barrier [4].

$$N(t) = N_0 \exp\left(-\int R\,dt\right) . \tag{2}$$

The QMFI readout current (for $\lambda = 69$ μm) is proportional to dN/dt and is a short pulse of charge. During the readout pulse, this charge is transferred to the load capacitor with a charge release time $\tau_P = 6.4$ μs (for $F = 0.35$ V/μm) [3]. Concurrently the capacitor decays with a decay constant ($\tau_D = RC = 4.8$ μs), where $R = 69$ kΩ and $C = 69$ pF are the effective load resistance and capacitance, respectively. The digitized signal fitted to the superposition of these rising and decaying functions is of the form

$$S = [\tau_D/(\tau_P - \tau_D)][P_0 \exp(-t/\tau_P) - D_0 \exp(-t/\tau_D)] \tag{3}$$

and is shown in Fig. 3. $P_0(1.1 \pm 0.5)$ and $D_0(1.0 \pm 0.5)$ are variables fitted to the signal. Defining S_0 as the value of the signal at $t = 0$ (beginning of readout pulse), it is

TABLE I. Comparison with other experiments.

Authors	Material	Concentration (FCI/atom)	Total sample mass (mg)
Smith *et al.* [15]	Niobium	$< 7.1 \times 10^{-20}$	6.5
Savage *et al.* [16]	Native Hg	$< 5.8 \times 10^{-19}$	2
Marinelli and Morpurgo [17]	Steel	$< 7.2 \times 10^{-20}$	3.7
This work	Si *p-i-n* diode	$< 2.3 \times 10^{-20}$	500

found that $S_0 = 0.26 \pm 0.29$, which corresponds to a signal voltage of $V_0 = 0.21 \pm 0.23$ μV. Since the input load capacitance is 69 pF, the charge ($Q = C \times V_0$) is equal to 90 ± 100 electrons.

Assuming a normal distribution we estimate the number of electrons in the readout pulse to be less than 293 with the confidence level 95%. The volume of the sample diode was 0.24 cm^3 with 1.23×10^{22} Si atoms. Hence the number of FCI's present is less than 2.3×10^{-20} per atom with 95% confidence level (see Table I).

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