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Electron-Drift Velocities in Argon-Boron Trichloride Gas-Mixtures

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Electron drift velocities were measured for argon gas mixtures containing 25 ppm to 0.5% boron trichloride additive using a pulsed-Townsend drift tube. These results show a marked sensitivity to mixture ratio and the gas mixtures also show negative differential conductivity and strong attachment at low electric field/gas number density.

I. INTRODUCTION

Recent interest in the reaction kinetics[1] and spectroscopy[1] of boron trichloride (BCl_3) gas and its dissociated products stems from its applications in the boron doping of silicon for semiconductors[2] and optical waveguides,[3] plasma etching of III-V compounds,[1,3–7] plasma deposition of boron,[4] and electric field measurements in plasmas.[5]

This article reports on electron transport in argon-boron trichloride gas mixtures, which are representative of those used in the above applications. Electron drift velocities were measured in binary gas mixtures composed of concentrations of BCl_3 in argon ranging from 2.5×10^{-5} to 5×10^{-3}. Analysis of the drift velocity in these gas mixtures at the higher concentrations of BCl_3 was complicated by anode current wave form changes and small signals due to the presence of negative ions formed by attachment.[1] Consequently a method of analysis was used which measured the swarm drift times in a rapid manner compatible with the automated experiment that permitted signal averaging and enhancement.

II. EXPERIMENTAL APPROACH

Traditionally, the arrival time of an electron swarm centroid can be identified by locating the half-fall point in the slope of the charge ramp. Levine and Uman used such an approach in their investigations of Ar, N_2, and CO_2 gas mixtures.[8] This technique locates the position on the charge ramp at which the derivative with respect to time (current) has fallen to half the maximum slope value and then subtracts the time of the signal onset (trigger position) to obtain the centroid transit time. The assumption is that when the current level falls to half of the maximum value, then half of the electrons have been absorbed by the anode, thus identifying the centroid (when longitudinal diffusion and boundary effects are neglected).

However, when electron drift velocity measurements were performed for Ar-BCl_3 gas mixtures, significant differences were observed in the charge response as compared to the typical integrated current ramp. This perturbation was attributed to two attachment processes:

$$e+BCl_3\rightarrow BCl_3^{-*} \quad \text{low energy electron attachment,} \quad \text{(I)}$$

$$e+BCl_3\rightarrow BCl_2+Cl^- \quad \text{dissociative attachment.} \quad \text{(II)}$$

There are significant differences in the literature regarding the cross section of the former process, however it is believed to peak near zero energy[1] and the BCl_3^- ion is metastable with a lifetime of about 60 μs.[1] The latter process has a threshold of approximately 1.0 eV.[1] At high mean electron energies greater than 1.5 eV, the attachment is attributed mainly to process II and at energies below 1 eV to process I.

Attachment reduced the drift current for some parameters as much as 40%. Petrovic *et al.*[1] previously experimented on attachment effects with argon-boron trichloride mixtures but did not report rate constant data because of the large influence of the BCl_3 on the electron drift velocity. The average electron energy of the swarm in pure argon ranges from 0.76 eV at $E/N=0.1$ Td (Townsend) to 5.8 eV at 20 Td. The addition of even small amounts of a molecular gas with large inelastic low energy cross sections significantly reduces the mean electron energy and in a Ramsauer gas such as argon increases the drift velocity.

The formation of negative ions (throughout the gap) causes a perturbation in the charge ramp and, of course, also affects the current ramp. The second derivative of the charge ramp produced the rate of change (dI/dt) of the drift tube current. By pinpointing the post-trigger minimum of this second derivative, the time position of the greatest charge was identified. The rate of change of the ion contribution is assumed to be small compared to the rate of change of the electron contribution, so that the difference between the trigger position and this minimum yielded the expectation transit time for the swarm electrons. This method is similar to that developed by Faidas *et al.*[9] for electron drift in dielectric liquids. The Christophorou group has also measured electron drift and attachment in BF_3 (Hunter *et al.*[10]).

III. APPARATUS

The apparatus used in the study is similar to that of Patrick *et al.*[11] A current-integrating (charge) preamplifier is used in conjunction with a pulsed-Townsend drift tube for analyzing electron swarm-induced current from which electron arrival times could be determined. The drift tube

[a]Deceased.

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system included a stainless steel chamber enclosing the drift space, an ultrahigh vacuum system, gas manifold, and signal acquisition electronics. The length of the drift space (photocathode to anode) was 6.45 cm, surrounded by 6 equally spaced guard rings with internal diameter of 5.6 cm.

Photoelectrons were generated in a pulsed-Townsend drift tube by a 10 ns UV pulse source (Xenon Corporation Nanopulser/Nanolamp) which illuminated a gold-palladium photocathode. The current pulse induced on the anode of the drift tube by the electron swarm was detected by a Tennelec TC174 current-integrating preamplifier. The resulting integrated current (charge) ramp was digitized by a Tektronix 2440 digital storage oscilloscope (DSO) and then passed to an IBM-PC/XT clone for storage and analysis through a general purpose interface bus (GPIB). High voltage bias was supplied to the drift tube by a Fluke 410B high voltage power supply. The gas pressure inside the drift tube chamber was measured with a Datametrics Barocel 621A pressure capacitance manometer.

IV. RESULTS & DISCUSSION

The electron drift velocities have been measured for pure argon using the second derivative of the charge measurement or the current derivative technique. Argon was selected as a test for the method because of its high mobility and its sensitivity to trace amounts of molecular impurity.[12] Electron drift velocity measurements were performed over an E/N (electric field/gas number density) range of 1×10^{-3} to 2.4×10^{1} Td and were found to be in excellent agreement with previous data.[13,14] Comparison of electron drift velocities determined by the traditional half-maximum (first derivative) and second derivative methods for pure argon revealed negligible discrepancy between the two methods. The agreement between the two techniques was found to be within experimental error.

Electron drift velocities were then determined for BCl_3-argon mixtures using the current derivative method and are shown in Fig. 1. The drift velocities increased from the argon data as the partial pressure of BCl_3 was increased.

The addition of boron trichloride to argon causes a decrease in the characteristic electron energy, and in effect, 'cools' the electron swarm by inelastic energy loss collisions with the BCl_3. However, the electrons are now in the Ramsauer–Townsend region of the buffer gas. The electron swarm has an increased mean free path and thus an increased drift velocity, although the swarm is now more anisotropic.

The electron drift velocities at very low E/N and/or high BCl_3 concentrations were unable to be taken reliably due to low current signal in those regions. The loss of signal at very low applied electric field was caused by excess loss of electrons due to electron attachment. This problem is not uncommon, as Petrovic *et al.*[1] also encountered a similar problem in their study of Ar-BCl_3 mixtures.

A study of helium-boron trichloride has shown an expected increase in drift velocity over the pure helium[15,16] case (Fig. 2). In addition, no evidence of negative differential conductivity was present. Therefore, it is believed that attachment *per se* of the boron trichloride was not the cause of the NDC in the Ar-BCl_3 mixtures, but rather the inelastic energy loss collisions.

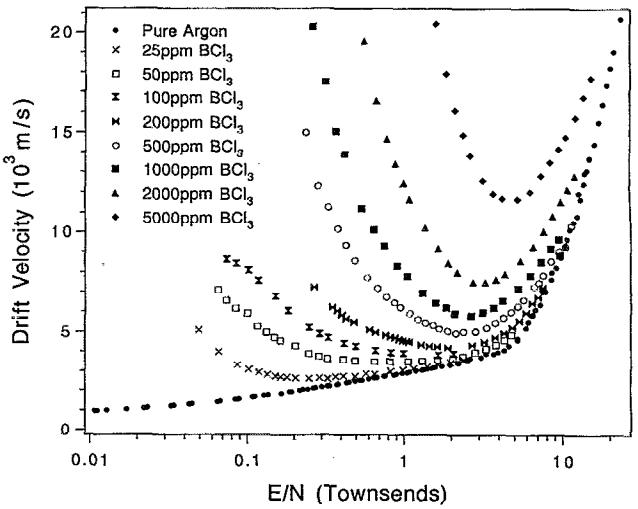

FIG. 1. The electron drift velocity as a function of E/N in mixtures of boron trichloride in argon.

V. CONCLUSION

Even at 25 ppm of BCl_3, electron attachment was observed. The swarm arrival time was measured using the current derivative method, which determines the greatest change of current with respect to time or the greatest electron flux at the anode, yielding what may be defined as the most probable or the expectation electron drift time. Electron drift velocities were determined using this technique for argon, each concentration of Ar-BCl_3 and He-BCl_3.

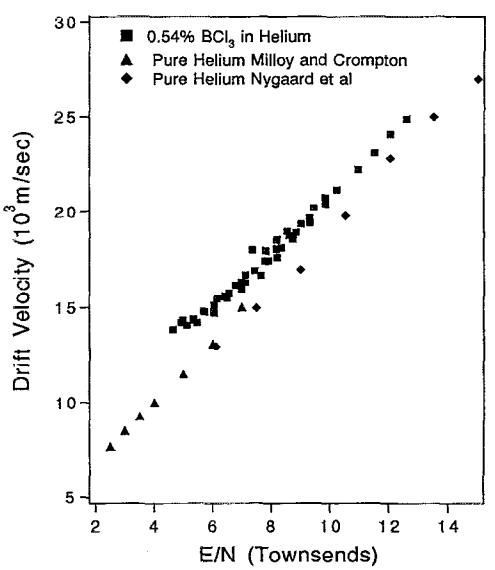

FIG. 2. The electron drift velocity as a function of E/N in a 0.54% boron trichloride-helium mixture.

The Ar-BCl_3 results obtained demonstrate regions in which the drift velocity *decreased* significantly with an increase in E/N. These results suggest large inelastic BCl_3 cross sections in the neighborhood of the buffer gas Ramsauer minimum. [The minimum is at approximately 0.23 eV, which is to be compared with the vibrational mode energies of 0.11 eV (Ref. 17)]. The large signal *amplitude* decreases at low E/N values demonstrating the effects of high attachment rates. The attachment effects are highest below the E/N values where sudden changes occur in electron mobility. These results suggest that the dominant attachment process is a direct attachment to BCl_3. The new results demonstrate that the electron drift velocity in argon-BCl_3 mixtures is very sensitive to the actual amount of BCl_3 and that the electron drift velocity increases monotonically with BCl_3 concentration up to 0.1% for E/N up to 2 Td.

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