

# ENHANCED ELECTRON ATTACHMENT TO HIGHLY-EXCITED MOLECULES AND ITS APPLICATIONS IN PULSED PLASMAS

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## Abstract

Studies conducted over the past several years have shown that electron attachment to highly-excited states of molecules have extremely large cross sections. We will discuss the implications of this for pulsed discharges used for H<sup>-</sup> generation, material processing, and plasma remediation.

## I. INTRODUCTION

By highly-excited states we specifically mean high-Rydberg (HR) states which have electronic binding energies of a fraction of an electron volt (eV). Rydberg states of atoms and molecules have some unique characteristics including long lifetimes and large cross sections for various collision processes [1]. In a molecule, energy can be stored in the vibrational/rotational degrees of freedom in addition to its electronic energy. Therefore, a neutral molecule may have a total internal energy exceeding its lowest ionization potential (IP); each vibrational/rotational mode will have a Rydberg series converging to its own IP, and these can be called "core-excited" Rydberg states. Recent experimental studies [2-4] have shown that molecules excited to a few eV above their lowest IP can have **microsecond**

or even higher.

Therefore, even if a fraction of molecules in a given plasma are excited to HR states, their collision processes may influence the properties of the plasma.

Our electron attachment studies on laser-excited HR states of molecules have shown that they have characteristically large cross sections for dissociative electron attachment; see **Fig. 1**

In pulsed discharges the conditions for electron attachment to HR states are optimized in the discharge "off" period, i.e., the afterglow: (i) the HR states of the molecules survive well into the post discharge due to their characteristically-long lifetimes, and (ii) the discharge electrons are rapidly cooled in the post discharge thus producing low-energy electrons that are conducive to electron attachment.

We will point out the possible implications of electron attachment to highly-excited states of molecules in three pulsed power technologies: (i) Generation of H<sup>-</sup> ions using H<sub>2</sub> discharges is actively being pursued due to the need for intense H<sup>-</sup> ion beams for magnetic fusion energy research. It has recently been shown that higher average H<sup>-</sup> beam currents can be extracted in a pulsed H<sub>2</sub> discharge source [9-14]; (ii) Recent studies show that power modulation enhances deposition/etching while reducing undesirable particulate formation in plasma processing discharges used in the processing of semiconductors [15-23]; (iii) Our recent studies [24] show that the energy efficiency in plasma remediation of volatile organic compounds in rare gas mixtures is enhanced in pulsed glow discharges. The above observations are likely to be related to enhanced dissociative electron attachment to HR states as described below.

## II. PULSED HYDROGEN DISCHARGES

Generation of H<sup>-</sup> ions using H<sub>2</sub> discharges is actively being pursued due to the need for intense H<sup>-</sup> ion beams for particle accelerators and for magnetic fusion energy research. Enhanced electron attachment to **vibrationally**-excited states of the ground electronic state of H<sub>2</sub> was reported [25, 26] at about the same time the efficient H formation in H<sub>2</sub> discharges was reported [27]. Ever since that time, an exhaustive experimental and theoretical effort has been devoted to understand the experimental observations in the H<sub>2</sub> discharge sources in terms of this electron attachment process (see, for example, [28]). However, recent studies [29-31] show that the experimentally measured H<sup>-</sup> number densities can not be completely accounted for by electron attachment to **high-vibrational (HV)** states. Based on our observations on

electron attachment to laser-excited  $H_2$  [32], we recently pointed out [33] that highly-excited electronic states of  $H_2$ , which are high-Rydberg (HR) states, populated in  $H_2$  discharges may account for the difference, also see [34, 35]. Evidence to support [36-38] and oppose [39] this proposal have been presented.

It has been recently shown [9, 10] that higher average H beam currents can be extracted by using pulsed discharges of  $H_2$ . Subsequent studies [11-14] have confirmed these observations and have presented further experimental observations designed to understand the reasons for this enhancement. Model calculations based on electron attachment to HV states yield  $H^-$  ion currents that are at least 4 times smaller than the experimentally-measured values [40].

We believe that the enhanced production of  $H^-$  signal in [12], as well as in the other pulsed  $H_2$  discharge experiments is due to, (i) the reduction in electron impact ionization of HR states, and (ii) the increased availability of slow electrons, in the post discharge. Further experiments are progress in our laboratory to test this hypothesis.

### III. PULSED MATERIAL PROCESSING DISCHARGES

Most plasma processing discharges use gas mixtures consisting of a "reactive gas" and an inert gas. Thus in addition to the population of excited states of the reactive gas by electron impact, they can also be populated by excitation transfer from metastable states of the inert gas as we have illustrated in recent experiments [6, 7].

By monitoring the electron decay time in the afterglow of a **silane/helium** pulsed discharge, Fleddermamm et al. [41] have shown that the dominant electron loss mechanism in the afterglow was dissociative electron attachment (non-dissociative electron attachment is not viable at the low pressures used in these experiments.) They estimated [41] a lower bound value of  $\sim 2.6 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$  for the electron attachment rate constant involved; yet this is an order of magnitude higher than the electron attachment rate constant corresponding to the measured electron attachment cross sections measured for the ground state of silane [42]. Fleddermann et al. [41] proposed that this enhanced electron attachment in the afterglow was to  $SiH_3$  or  $SiH_2$  radicals that were produced during the discharge. However, this possibility can be ruled out as shown below.

Negative ions from a pulsed silane discharge have been mass identified recently by Howling et al. [43, 44]. They reported that monosilicon negative ions are initially produced by electron attachment and subsequently these polymerize to produce polysilicon negative ions; the dominant monosilicon negative ion produced by electron attachment is  $SiH_3^-$  [43, 44]. Since it is not possible to produce the  $SiH_3^-$  ion via *dissociative* electron attachment to  $SiH_3$  (non-dissociative electron attachment is weak under

low-pressure conditions) or  $SiH_2$  radicals, it is clear that the enhanced production of  $SiH_3^-$  ion in the afterglow must come from the parent  $SiH_4$  molecule. Since the ground state electron attachment for silane is more than an order of magnitude smaller than the experimentally measured value in the afterglow of a pulsed discharge [41], the only other explanation is dissociative electron attachment to **highly-excited** states of silane. This is also consistent with our recent observation [5] of large electron attachment rate constants of the order of  $10^{-7} \text{ cm}^3\text{s}^{-1}$  for highly-excited states of silane produced via laser irradiation.

In plasma processing of semiconductor materials, it has been shown that pulsed discharges yield faster deposition with improved film quality [16-18, 20, 23, 45] and faster etching with reduced notching [15, 21, 46-49].

This enhanced performance could be due, partly, to the enhanced dissociative electron attachment that occurs at the falling edge of a pulse. Dissociative electron attachment leads to the formation of radicals and fragment negative ions (which are *charged radicals* that can contribute to *anisotropic etching* as well as deposition). In a cw discharge, the negatively-charged particles are trapped in the discharge due to the sheath potentials and are allowed to grow into particulates. (Thus, the negative ions are also prevented from contributing to deposition/etching). Once they become micrometer-size particulates, the viscous drag force becomes large enough to overcome the electrostatic forces and they can reach the substrate. Therefore, the cw operation of the discharge is detrimental in two ways: (a) it prevents the negative ions from reaching the substrate and thus possibly contributing to the etching/deposition (furthermore, in etching applications the negative ions that reach the substrate can neutralize the positive ions, and thus reduce "notching"), and (b) it traps the negative ions in the discharge, thus allowing them to grow to pm-size particulates.

*By time-modulating the discharge, the negative ions populated during the "on-time" are allowed to reach the substrate during the "off-time" (when the sheath fields are collapsed) and thus deposition/etching is enhanced while, at the same time, particulate growth is prevented.* In addition, the negative-ion formation itself may be enhanced at the time the discharge is turned off and thus the flux of negative ions to the substrate is further enhanced during the discharge off period.

### IV. PULSED PLASMA REMEDIATION

We recently studied the destruction of benzene in a **benzene/Ar** mixture subjected to a pulsed glow discharge [24]. The destruction efficiency was observed to be much improved compared to a DC glow discharge [50]. Diagnostic spectroscopic measurements indicated that excitation transfer from the metastable states of Ar to benzene in the afterglow of the discharge was primarily

responsible for the destruction of benzene.  
Furthermore, in these experiments

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