ION-X Dopant Gas Delivery System Performance Characterization at Axcelis

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***Abstract*— The performance of ION-X delivering arsine (AsH_3), phosphine (PH_3), and boron trifluoride (BF_3) was evaluated at the Axcelis Advanced Technology Center. ION-X is a sub-atmospheric dopant gas delivery system specifically designed for ion implantation, and the first commercial product that uses Metal-Organic Framework (MOF) materials. MOF materials are a new class of adsorbents with unprecedented surface areas and uniform pore sizes that can be precisely customized to the specific properties of electronic gases. ION-X cylinders were installed in high current implanters and their performance was compared to the incumbent UpTime® gas delivery systems. In all cases, the target dose was 5×10^{15} at/cm^2 with beam energies of 40 keV, 20 keV and 15 keV for As^+, P^+, and BF_2^+ ion implants respectively. In-process and on-wafer results of the MOF-based dopant gases compared positively to conventional source gases. The issue of metal contamination was investigated in detail. Specifically, beam and wafer contamination levels (both surface and energetic) were evaluated and compared to the reference qualified products. In all cases the metal levels were below specification limits matching the performance of the ultra-high purity reference product.**

Keywords—ION-X, MOF; sub atmospheric gas source; ion implantation; dopant gases; arsine, phosphine; hazardous gas; NuMat Technologies

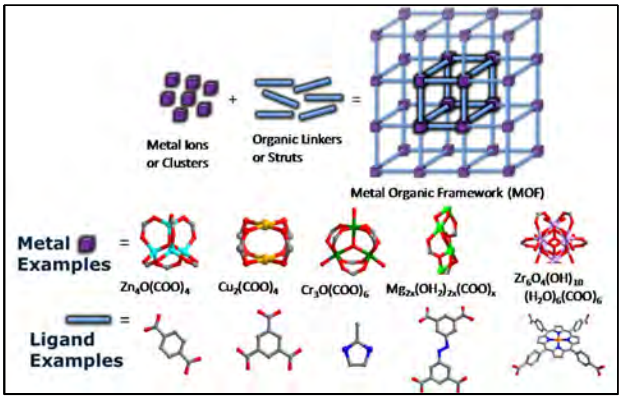

Fig. 1. MOF Structure and composition examples

I. INTRODUCTION

The storage and delivery of dopant gases in ion implantation creates significant environmental, health, and safety challenges. Their use requires implementation of stringent safety control systems to minimize the risks of exposure to humans and the environment. In the early days, implant users utilized heated sources to introduce metal vapors into the ion source. Plagued with issues related to dose control and condensation, the industry transitioned to high-pressure gas cylinders. Due to their lethality, hydride gases (primarily arsine and phosphine) were diluted with hydrogen gas while boron trifluoride was delivered in neat concentrations. The concept of delivering dopant gases from adsorbed sub-atmospheric sources appeared in 1993 when ATMI (now an Entegris company) introduced SDS®, a different approach to reduce the toxic gas storage hazards [1]. The technology involves the use of high surface area adsorbents to condense the gas molecules onto their surfaces. This process effectively reduces the pressure inside the cylinder while maintaining storage capacities comparable to high pressure systems. In order to improve safety, these vessels are filled to sub-atmospheric pressures (measured at room temperature) in order to inhibit an outward gas release in the event of a leak. The gases are weakly bound to the surface of the adsorbents allowing their delivery using the pressure differential driven by the high vacuum inside the implanter. SDS® revolutionized the way dopant gases were delivered and advanced the adsorbent technology with the release of thee product generations: zeolite-based SDS®1, beaded activated carbon SDS®2, and monolithic carbon SDS®3. Powered by the safety and productivity advantages and with the support of OEMs and end-users SDS® was quickly adopted by the ion implant community. Approximately a decade after the introduction of SDS®, the gas delivery technology took another evolution step with the introduction of mechanically-based gas delivery systems. VAC® (developed by ATMI now an Entegris company) and UpTime® (Praxair) use valves and pressure regulators inside high-pressure gas cylinders to actuate and deliver dopant materials only when the downstream pressure is sub-atmospheric. While the gas contents in the cylinder are pressurized, the mechanical-based systems effectively reduce the delivery pressure lowering the risks of toxic gas exposure.

In this paper, we describe a new phase in the evolution of hazardous gas storage with the introduction of ION-X®, a next generation sub-atmospheric gas delivery system. ION-X utilizes a novel ultra-high surface area class of materials called metal-organic frameworks (MOFs). The article provides an overview of the new adsorbent properties and features compared to legacy materials. In addition, the implant process performance of the new product delivering arsine, phosphine, and boron trifluoride evaluated at Axcelis will be described

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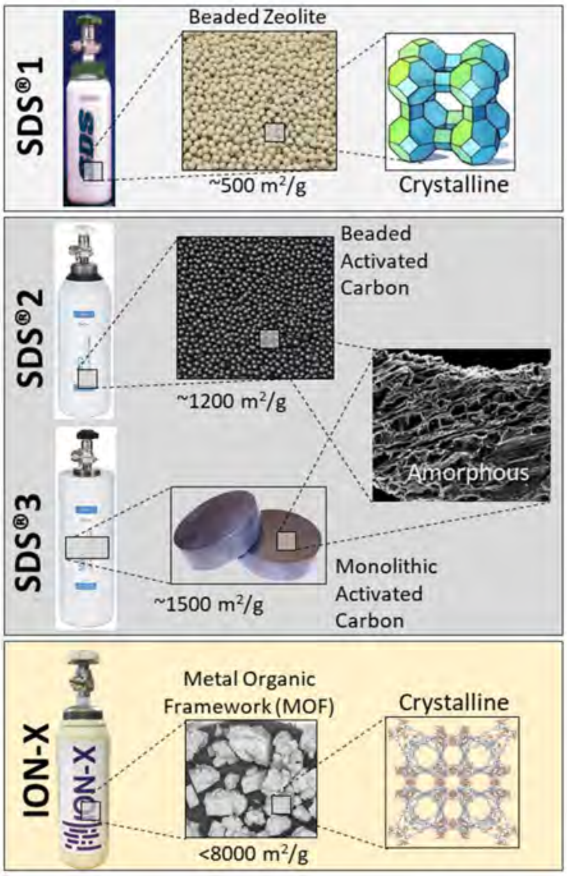

Fig. 2. Structural and physical properties of adsorbent materials used to store and deliver ion implant dopant gases

II. MOF INTRODUCTION

MOF are three-dimensional crystalline structures built with metal-containing nodes connected by organic links (Fig. 1). The resulting highly organized molecular structures generate nano-pores with record surface areas [2-4]. In addition, the large number of available metal nodes and organic linkers provide significant molecular design flexibility. For instance, scientists can tailor the chemical and physical properties of the adsorbent material to fit the application. MOFs are one of the fastest growing class of materials, with thousands of experimental structures now being reported. Since their discovery in the early 1990's, MOFs have transitioned from an academic curiosity to a widely recognized new type of materials with practical applications in energy, specialty chemicals, military, medical, pharmaceutical, and electronics industries.

For gas storage and delivery applications, MOFs provide advantages over traditional adsorbents (Fig. 2). Their design versatility facilitates fine tuning of pore size, surface area, chemical stability, and adsorption/desorption characteristics specific to the properties of the adsorbed gases. MOFs routinely surpass the surface areas of zeolites and activated carbon adsorbents (with up to 8,000 m^2/g has been reported) [5]. The ability to fine-tune the MOF pore size is important in order to match the dimensions of the MOF cavity to the molecular size of the target adsorbate. Combined with surface energy optimization, these factors impact adsorption capacities (how much gas can be loaded) and desorption characteristics (how much can be delivered as a function of pressure). Unlike the broad pore size distributions found in activated carbon adsorbents, MOFs' crystallinity results in more "usable" pores. This pore size uniformity also results in higher gas quality, as impurities are selectively size-excluded. To manage the structural diversity and minimize time-consuming laboratory work, NuMat employs computer design simulations to down-select the best MOFs for a specific application. The model uses a database of hundreds of thousands of theoretical structures to screen the highest performance adsorbent for an application of interest. This process allows for structure selection that would take many years in the laboratory to be condensed to the timescale of days.

Dopant gas purity and stability are extremely important in ion implant applications. Adsorbent/gas interactions can be a contributing factor to gas decomposition, leading to impurities and unwanted dopant gas composition rates. With zeolites and carbon adsorbents, reactivities towards adsorbed gases are hard to control due to their limited molecular flexibility (typically restricted to carbon, aluminum, and silicon and their oxides). MOFs, on the other hand, can be synthetized from a large range of organic and inorganic constituents offering more options for creating stable gas/adsorbent interactions. The stability of the selected MOF adsorbents loaded with hydride gases and BF_3 was studied extensively as part of the development of ION-X [6]. Accelerated stability tests performed at elevated temperatures demonstrated no degradation of MOFs or generation of gas and metal impurities. MOF stability and dopant gas purity were verified by Infineon in manufacturing-like environments [7]. In a separate set of reliability tests, multiple adsorption and desorption cycles showed loading and deliverable performance variations of less than 1% through a 10-year period.

III. ION-X: MOF-BASED DOPANT GAS DELIVERY ADVANTAGES

ION-X is a sub-atmospheric dopant gas storage and delivery system designed for ion implantation. ION-X uses granulated (not monolithic) MOF adsorbents with tailored pore sizes to

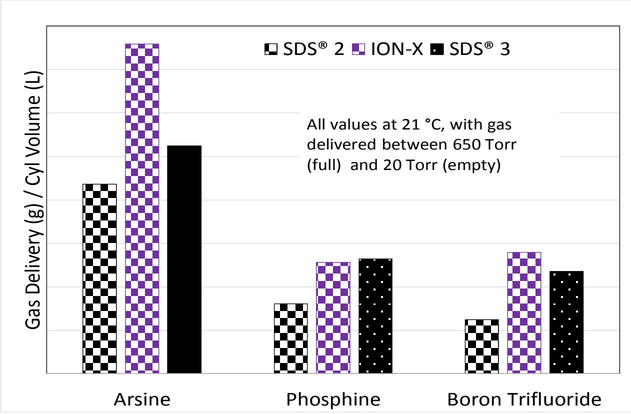

Fig. 3. Volumetric dopant gas delivery comparison between ION-X and activated carbon-based products

effectively and reversibly adsorb arsine, phosphine, and boron trifluoride gases. Each MOF material was custom designed to match the physical and chemical properties of the dopant gases. Unlike mechanically-based dopant gas delivery systems, the pressure in full ION-X cylinders is below one atmosphere significantly reducing the health and environmental impact of an accidental gas release. Due to their high toxicity at low concentrations, this added safety factor is especially important when handling hydride gases. As shown in Fig. 3, the superior surface areas and uniform structures of MOFs provide capacity and deliverable advantages compared to existing carbon adsorbent-based products. Measured against the granulated activated carbon-based SDS®2, ION-X provides 45% higher gas deliverables (averaged for the three dopant gases). Even when using the high bulk density (monolithic) carbon adsorbent in SDS®3, ION-X delivers 30%, more AsH_3, 15 % more BF_3, and approximately equal amount of PH_3 gas.

IV. IMPLANT PROCESS EVALUATION

The performances of ION-X dopant delivery systems were recently evaluated using a PurionH 300 mm high current ion implanter at Axcelis' Advanced Technology Center (Beverly, MA, USA). The test plan included flow, mass spectral, and metal contamination analyses (both at the surface and at implanted depth). The experiments were repeated using commercially available UpTime® (an adsorbent-free well-established sub-atmospheric dopant gas source) in order to provide a basis for comparison.

Cylinder installation and setup was seamless, requiring no modifications to the existing gas box hardware or software. Flow rate stability for all three dopant gases (AsH_3, PH_3, and BF_3) was demonstrated in the 3.5 to 8 sccm ranges down to cylinder pressures of 20 torr (spec limit). For arsine, the gas delivery continued through a full cylinder depletion, showing a stable flow rate down to a cylinder pressure below 3 torr.

The beam energy, purity, and stability were evaluated by analyzing the mass spectra generated during the implantation processes. In all cases, the target dose was 5 x 10^{15} at/cm^2 with beam energies of 40 keV, 20 keV and 15 keV for As^+, P^+, and BF_2^+ ion implants respectively. The stability and purity of all ion beams were within specifications and very similar to the ones produced by the reference gas sources. Based on their mass spectra, ION-X did not generate any impurities derived from either gas or MOF decomposition.

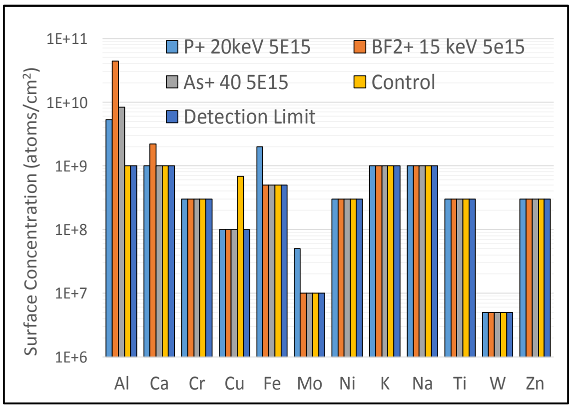

Fig. 4. Selected metal surface contamination of wafers implanted using ION-X compared to

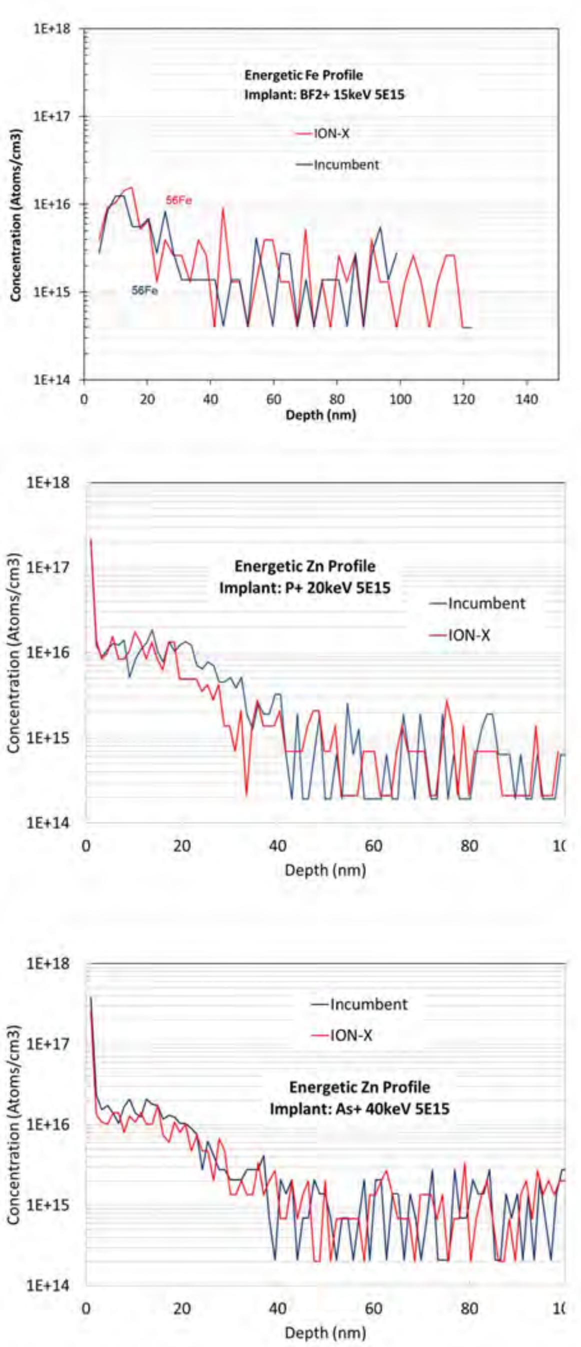

Fig. 5. Comparison of SIMS Profiles of Zn (hydrides) and Fe (BF_3) levels using incumbent and ION-X gas sources.

Neutral and energetic metal contamination levels were thoroughly investigated in this study. All metal analyses were performed by sampling wafers produced using the recipes described in the previous paragraph. Vapor Phase

Decomposition-inductively coupled Plasma-Mass Spectrometry (VPD-ICP-MS) was used to monitor the contamination from key trace metals at the wafer surface. Particular attention was given on monitoring zinc and iron, as these metals are used in the hydride and BF_3 ION-X MOF adsorbents respectively. Results show that all surface metal levels were within specification limits and compared well to the levels detected in control wafers (Fig. 4). In all cases, zinc and iron surface contamination levels were below their corresponding detection limits of 0.03 and 0.05 x 10^{10} atoms/cm^2.

Energetic metal contamination is of special interest in ion implantation as even low levels of impurities could affect the performance of the electronic devices. The depth profiles of the metals used in the ION-X MOF's composition were measured using Secondary Ion Mass Spectrometry (SIMS). Wafers used for SIMS analyses were doped utilizing both ION-X and incumbent gas sources implanted by the same tool and using the previously stated recipes. The zinc and iron metal concentration profiles for the hydride and boron implants were well within specifications and show no discernable differences between the incumbent and the MOF-based gas sources (Fig. 5). These results, combined with the previous surface contamination tests, conclusively establish the satisfactory gas and ion purity of the dopant species extracted from ION-X adsorbents. Moreover, the results are consistent with extensive gas analyses performed at NuMat after subjecting the MOF adsorbent materials to accelerated aging, vibration, and cycle testing.

V. CONCLUSIONS

This article provides process and on-wafer performance of ION-X, a new MOF-based dopant gas delivery system. The adsorbents used in these cylinders have surface areas, stability, purity, and pore sizes ideal for the storage and delivery of ion implant dopant gases. In-process and on-wafer performance of boron trifluoride, arsine, and phosphine dopant sources compared positively to conventional source gas cylinders. The issue of contamination was investigated in detail, demonstrating that the new adsorbents do not contribute to surface or energetic metal impurities. The results published in this paper provide independent evaluation of the new product, supporting its safe use in mainstream ion implant applications. To that end, ION-X is already qualified and being used at an electronics manufacturing site with confirmed high stability and purity performance.

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