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Review

Expanding the dimensions of metal–organic framework research towards dielectrics

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ABSTRACT

Metal–organic frameworks (MOFs) belong to a class of hybrid materials that are unparalleled in their degree of structural diversity and functional tunability. The construction of these crystalline materials promise to advance the burgeoning field of ultra-low dielectrics. The rapid development of ultra-large-scale integration (ULSI) and the continuous miniaturization of feature sizes of integrated circuits approaching the nanometer (nm) scale, suggest that ultra-low dielectric constant materials will be needed, instead of the traditional SiO_2 (κ = 3.9). Appropriately designed MOFs promise to be the next generation of interlayer low-dielectric materials with the potential to be extremely porous, inert, and insulating. This review discusses our comprehensive investigations of obtaining low-κ MOFs and provides the current state of MOF research for dielectric applications. The design principles that are required to develop low-dielectric MOFs and structural elements that influence their behavior, as well as the integration of MOFs into metal–insulator–metal (MIM) devices are discussed.

Contents

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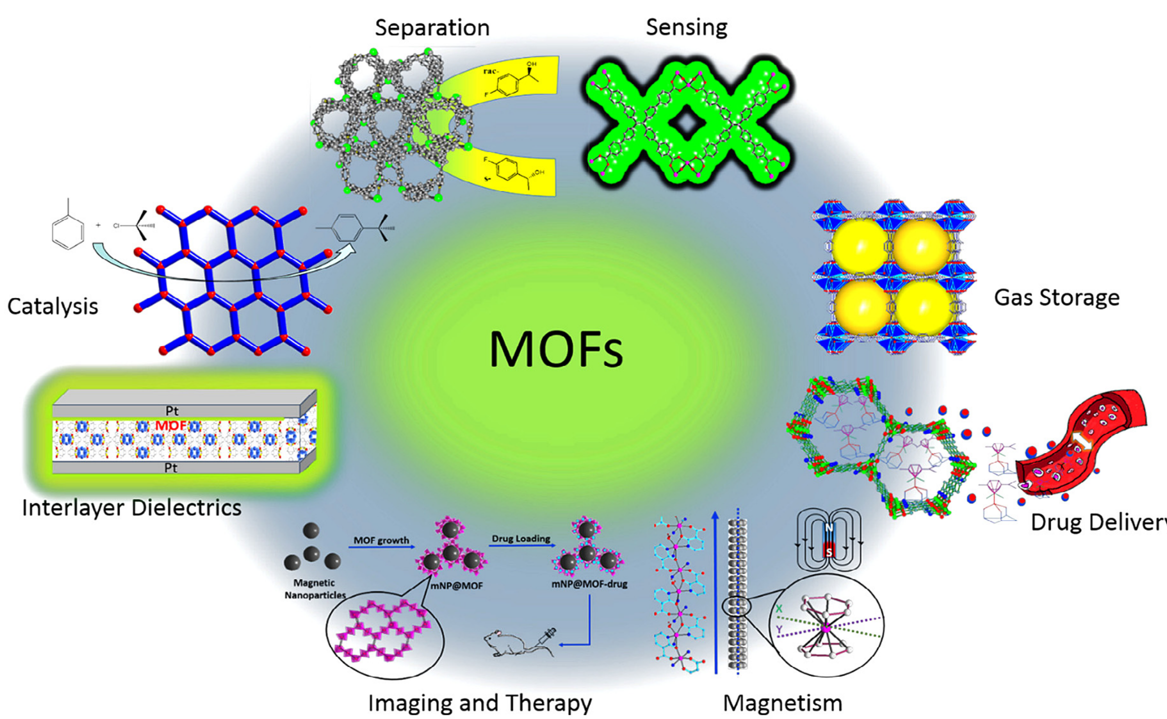
1. Introduction

Metal–organic frameworks (MOFs) belong to a family of hybrid materials that possess highly uniform structures, excellent porosity, with surface and structural properties that can be easily tuned. MOFs have been extensively studied over the past decade for applications in gas storage, sensing, chemical separation, catalysis, drug delivery and biomedical imaging (Scheme 1) [1–11]. The construction of these ordered materials has also led to dramatic innovations in the field of magnetic, opto-electronics and ferroelectric materials [12–18]. The combination of long-range order and synthetic flexibility have inspired many research groups to explore the possibility of including these materials in novel electronic devices such as field effect transistors, photodetectors and light harvesting solar cells [19–23].

According to Moore's law, the number of active devices on an integrated circuit (IC) has been doubling at about two year intervals [24,25]. With the continuous shrinking of device dimensions and an ever-increasing number of active devices on integrated circuits (ICs), interconnect resistive–capacitive (RC) delay and electronic cross-talk has become a major issue and poses serious limitations to device performance [26–29]. RC delay decreases by using metals with low resistivity, while the issue of cross talk between the interconnecting wires, could be eliminated by the introduction of low-κ ILD materials. According to the International Technology Roadmap for Semiconductors (ITRS), porous materials and air gap structures will take the place of the currently used low-κ materials (SiO_2) in multilevel interconnect schemes in the near future [30]. Since then, the design and synthesis of new low dielectric constant (low-κ) materials has been a subject of interest in terms of their potential as interlayer dielectrics (ILDs) for use in high-performance electronic devices. Early generations of low-κ dielectrics were obtained by doping the traditional SiO_2 with fluorine and carbon during the chemical vapor deposition (CVD) of the materials [27,31]. Studies dealing with the preparation of carbon-based materials, fluorinated amorphous carbon, benzoxazine-based polymers, polyarylene, polyimides and polyhedral oligomeric silsesquioxanes for use as low-κ materials in interlayer dielectrics have appeared recently [26,32–42]. Introducing porosity into silica-based materials can also reduce the dielectric constant to that for a next generation of dielectric material with a κ value between 2 and 3 [43–45]. As air has the lowest dielectric constant ($\kappa = 1$) so partially replacing solid materials with air or vacuum would be a viable route to developing new low-κ materials [46]. It would open up a path for new materials, such as MOFs, to be used as low dielectric materials and to take advantage of their porous and insulating nature to construct interconnects and interlayer dielectrics (ILDs). In these examples, the MOF would play a significant role in insulating, regressing, and blocking the charge in integrated chips [47–57].

Some electrically conductive MOFs have been reported recently by Allendorf and Talin (HKUST-1), Dincă (TTFTB containing frameworks, NiHITP, NiHIB, and copper analogs), Marinescu and coworkers (CoHTTP), and semiconducting MOFs have been reported by the research groups of Lu, Garcia, Manimaran, Volkmer, etc. [58–71]. However, the low electrical conductivity of MOFs arising



Scheme 1. Myriad applications of metal–organic frameworks make them promising future materials.