Chapter

Solid State Humidity Sensors

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Abstract

A variety of humidity sensors have been developed to address the problem of humidity measurement in instrumentation, agriculture and systems which are automatic. Various types of humidity sensors have been reviewed along with their mechanisms of humidity detection. Thin and thick film preparation processes are quite flexible. This flexibility provides advantages over other technologies. After comparing all the aspects of different humidity sensors, it has been observed that there are still some shortcomings left, which need to be removed to enhance the humidity sensing capability, recovery and response times of the sensor elements.

Keywords: Humidity sensors, Relative humidity, thick/thin film, Fabrication technologies, capacitive/resistive sensors, protonic conduction mechanism

1. Introduction

Significant improvements have been seen in the sensor technology in recent years. The miniaturisation process provides a wide range of advantages to the field of sensor technology [1–11]. It is a well known fact that humidity plays a significant role in all the processes occurring on this planet. For the high efficacy of all these processes, the monitoring, detection and control of the humidity of the surroundings is of utmost importance [12, 13]. For the fabrication of good humidity sensors, choice of fabrication technologies, optimisation of the surface for conductance and cost are the major factors that play a very important role [14–27].

1.1 Basics of humidity

"Humidity is defined as the amount of water vapour in an atmosphere of air or other gases". The units of humidity parameters depend on the technique used. In this respect, "Relative humidity (RH)", "Parts per million (PPM)" by weight or by volume and "Dew/Frost point (D/F PT)," are used.

In addition to the above units, it is worthwhile to mention three more parameters and their relationships here.

i. Absolute Humidity: It is defined as a ratio of the mass of water vapour in air to the volume of air. It is also called vapour density and its units are g/m^3 or $grains/ft^3$. The absolute humidity is given by

$$AB = m/V, \text{ where 'm' is the mass of water vapour and 'V' is the volume of air.} \quad (1)$$

ii. Relative Humidity: It is defined as ratio of the amount of moisture content of air to the maximum (saturated) moisture level that the air can hold at a same

given temperature and pressure of the gas. It is denoted by RH and depends upon the temperature and is a relative measurement.

$$\text{RH (in percentage)} = \text{Pv} \times 100 / \text{Ps}, \text{ where Pv is the actual partial pressure of the moisture content in air and Ps is the saturated pressure of moist air at same given temperature.} \quad (2)$$

Saturation Humidity: It is defined as the ratio of the mass of water vapour at saturation to the volume of air. It is denoted by SH.

$$SH = m_{ws} / V \quad (3)$$

SH is the saturation humidity (g/m^3), m_{ws} is the mass of water vapour at saturation (g) and V is the volume of air (m^3). The saturation humidity is a function of temperature. SH is a function of temperature and can provide the maximum amount of moisture content (mass) in a unit volume of gas at a given temperature.

The percentage relative humidity can also be expressed as.

$$\text{RH (In percentage)} = AB \times 100 / SH \quad (4)$$

Parts per million by volume (PPMv) is defined as volume of water vapour content per volume of dry gas and parts per million by weight (PPMw) is obtained by multiplying PPMv by the mole weight of water per mole weight of that gas or air. PPMv and PPMw are the absolute humidity measurements.

Dew point is defined as a temperature (above 0°C) at which the water vapour content of the gas begins to condense into liquid water, and Frost point is the temperature (below 0°C) at which the water vapour in a gas condenses into ice [28, 29]. D/F point parameters depend upon the pressure of the gas but are independent of the temperature. The ambient relative humidity is given by.

$$\text{Ambient relative humidity} = \text{Ambient temperature} - \text{Dew point temperature} \quad (5)$$

2. Classification of humidity sensors

Depending upon the different operating conditions, a variety of humidity sensors have been developed in due course of time. Based on the units of measurement, absolute humidity and relative humidity, humidity sensors have been divided into two classes, which are explained as follows:

i. Relative humidity (RH) sensors

ii. Absolute humidity sensors (hygrometers)

It is worthwhile to mention here that relative humidity sensors are preferred over absolute humidity sensors. The RH sensors are classified into three classes: Ceramic type (based on semiconducting materials), organic polymer based sensors and organic/inorganic hybrid sensors (based on polymers and ceramic materials). All the above mentioned categories make use of changes in the physical and electrical properties of the sensor elements, when exposed to different atmospheric humidity conditions of the surrounding environment. They provide a measure of humidity depending upon the adsorption and desorption of water molecules.

In hygrometer type of sensors, humidity measurement is determined by either measuring the conductance or capacitance of the sensing material, when it is exposed to the environmental humidity [30–33].

The first electrolytic humidity sensor was developed by Dunmore based on Lithium Chloride (LiCl) in 1937. A porous supporting material was immersed in a humidity sensitive partially hydrolysed polyvinyl acetate which was impregnated with LiCl solution and a potential difference was applied across the supports to form an electrolytic cell. By absorbing the water vapours via the porous medium, the ionic conductivity of the cells was changed and humidity was detected [34–36]. These types of sensor elements suffered from the following types of drawbacks, which led to the development of impedance-sensitive humidity sensors [37–41]:

- Low response times
- Low recovery times
- Not reliable to work in conditions, which has high moisture content

The organic polymer film humidity sensors can be divided into resistive and capacitive types [42–44]. The resistive type sensors can be divided into electronic and ionic conduction type. In the electronic conduction type of sensors, polyelectrolytes respond to water vapour variations by changing their resistivity. On the other hand, in the ionic conduction type, variation of the dielectric constants of the polymer dielectrics changes the capacitance of the material and hence the humidity is measured.

Ceramic type humidity sensors based on metal oxides have clear advantages over their other counterparts such as good mechanical strength, thermal capability, physical stability and resistance to corrosive chemicals.

Depending upon the sensing mechanisms, ceramic type sensors can be divided into:

- Impedance type
- Capacitive type

The impedance type of sensors can be further subdivided into ionic conduction and electronic conduction types and work by observing the changes in the conductivity of sensor elements, when they are exposed to different levels of humidity. [45, 46].

The metal oxide ceramics elements are prepared by various conventional and advanced ceramic processing methods, with an aim to produce porous structures that support adsorption of water vapours from the surrounding atmosphere.

3. Principle of protonic-conduction type ceramic humidity sensors

A variety of humidity sensing mechanisms have been proposed by various research investigators for the humidity sensing by ceramic based sensors. The mechanisms of humidity sensing via ionic conduction, electronic conduction, solid electrolyte and capacitive types are based on water vapour adsorption either by chemisorption, physisorption or capillary condensation processes. As water molecules are absorbed on the surface of the sensor elements, so it is worthwhile to discuss about the hydrogen ion (H^+) and hydroxide (OH^-) ion diffusion into the sensor elements [47–51].

3.1 Hydrogen (H^+) ions diffusion

This proton transfer mechanism was first proposed by Grotthuss. In this mechanism, protons are tunnelled from one water vapour molecule to the next water vapour molecule through hydrogen bonding as shown in the **Figure 1.**

In the proton carrier mechanism of ceramic humidity sensors, the adsorbed water molecules condense on the thin film surfaces or in bulk and protons carry out the conduction process [52, 53].

3.2 Diffusion and mobility of hydroxide (OH^-) ions

On the similar lines of proton transfer, Grotthuss suggested another mechanism for the hydroxide ion transfer. According to this mechanism, the mobility of the hydroxide ions also occurs through proton transfer mechanism as shown in the **Figure 2.**

An auto ionisation reaction of the water vapours occurs on the surface of the sensor element due to amphoteric nature of water molecule. In this process, a water molecule becomes hydroxyl ion with the loss of a hydrogen ion. The released hydrogen ion donates the proton to another water molecule to form hydronium ion with has a formula H_3O^+.

At low humidity levels, the charge carriers are predominantly protons.The protons are transferred through hopping of hydrogen ions between the sites that have hydroxide ions present on them. At higher humidity levels, as more water layers are present, more dissociation of water molecules occurs to produce hydronium ions. When the thin film surface is completely covered with water molecules, diffusion of hydronium ions on hydroxide ions dominates. In addition to this, the proton transfer by hydroxide ions between the adjacent water molecules also occurs. This charge carrying continues when hydronium ion transfers a proton to a neighbouring water molecule and forms another hydronium ion. The mechanism involves the

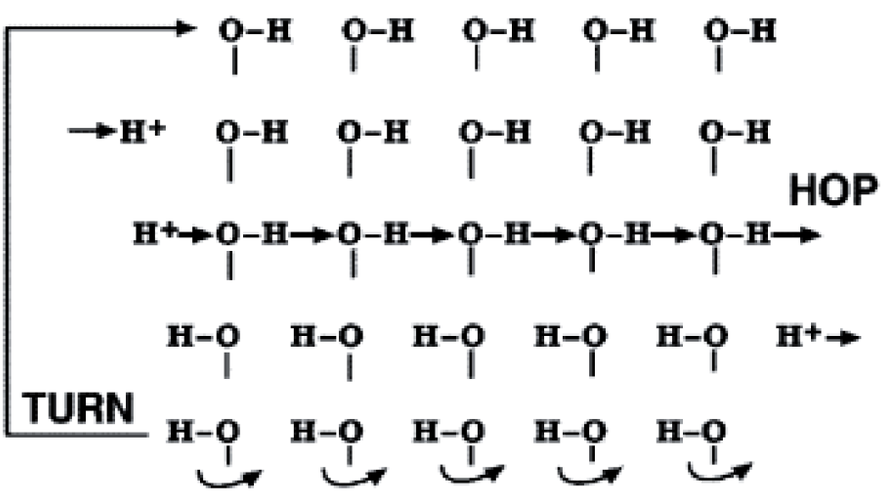

Figure 1.
Proton conduction of the hydrogen bonded networks between water molecules [54].

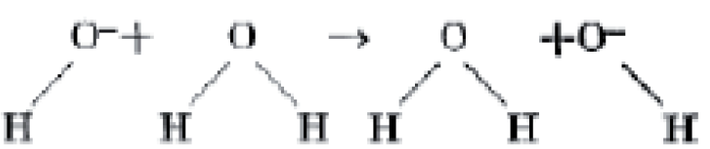

Figure 2.
Proton transfer mechanism of hydroxide ions.

dancing of protons from one water vapour molecule to the another water molecule. This leads to the change in resistance and capacitance of the thin film elements [55].

3.3 Water adsorption and conduction mechanism on ceramic oxide solid surfaces

It is well known that the surfaces of most of the metal oxides are covered with hydroxyl groups, when exposed to the humid atmospheres. This results in the formation of hydrogen bonds that facilitates the absorption of water molecules by ceramic oxide surfaces as shown in **Figure 3.** The formation of these hydrogen bonds results in the change of electrical conductivity of the surfaces.

Interaction of water molecules with ceramic oxide surfaces is a three step process, which are explained below:

In the first step, a few water vapour molecules are chemically adsorbed at the neck of crystalline grains on the activated sites of the surface. This leads to the dissociation of water vapour molecules to form hydroxyl groups. In this interaction, protons are generated which migrate from one site to another site on the surface and react with oxygen ions to form a second hydroxyl group as shown in the **Figure 4.**

In the second stage, more water vapour layers are physically adsorbed on the first stage formed hydroxyl layer, forming multilayers. The multilayers are more disordered than the first monolayer.

In the third stage, with the formation of more layers, a large amount of water molecules are physisorbed on the necks and flat surfaces. Therefore, singly bonded water vapour molecules have higher mobility and form continuous dipoles and electrolyte layers between the electrodes. This results in the increased dielectric constant and bulk conductivity. The multilayer formation of water vapour molecules

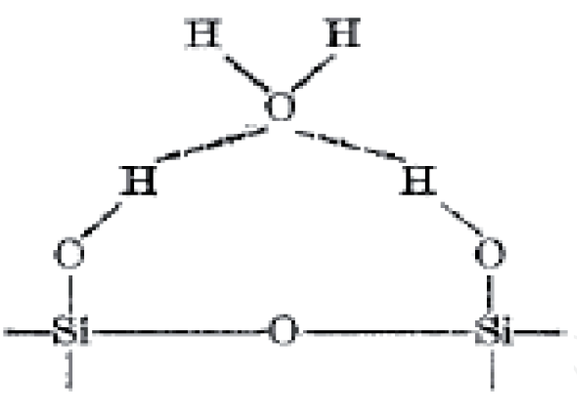

Figure 3.
The above diagram shows the adsorption sites on the silica surfaces and formation of hydroxyl pairs to hold water molecules.

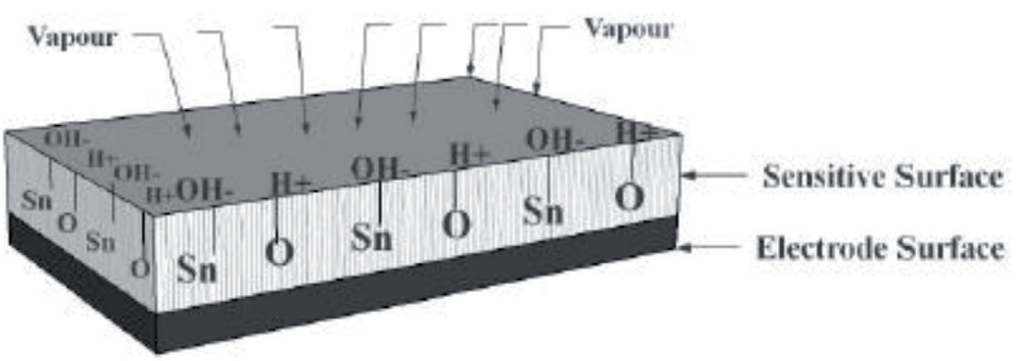

Figure 4.
Illustration of water vapour chemisorptions and hydroxyl layer formation on the surface of tin oxide.

on ceramic surfaces is confirmed by the increase of dielectric permittivity of the surface and is shown for iron oxide in the given **Figure 5.**

It has been found out that physisorption of water occurs at temperatures <100°C while chemisorptions occurs in the temperature range of 100-400°C. In this temperature range, hydroxyl groups interact with the surface of ceramic material [56–69].

The porous structure of the ceramics is mainly responsible for the physisorption of water vapours on the surfaces of humidity sensors, which are based on ceramic materials [70, 71]. For the cylindrical pores in the ceramic materials, the radius of the pores is given by the Kelvin Equation [72].

$$r_k = 2\gamma M / \rho RT \ln\left(p_s / p\right) \quad (6)$$

r_k is called Kelvin radius of the cylindrical pores. γ,M and ρ are the surface tension, molecular weight of water and density respectively. p is called the vapour pressure of water and p_s is vapour pressure of water at saturation. R is called gas constant and T is called the absolute temperature [73].

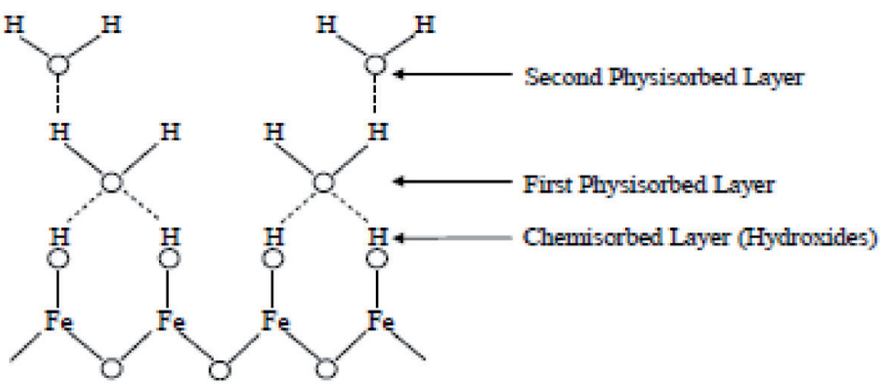

Figure 5.
The above diagram shows the multilayer structure of adsorbed water vapour molecules on the surface of iron oxide.

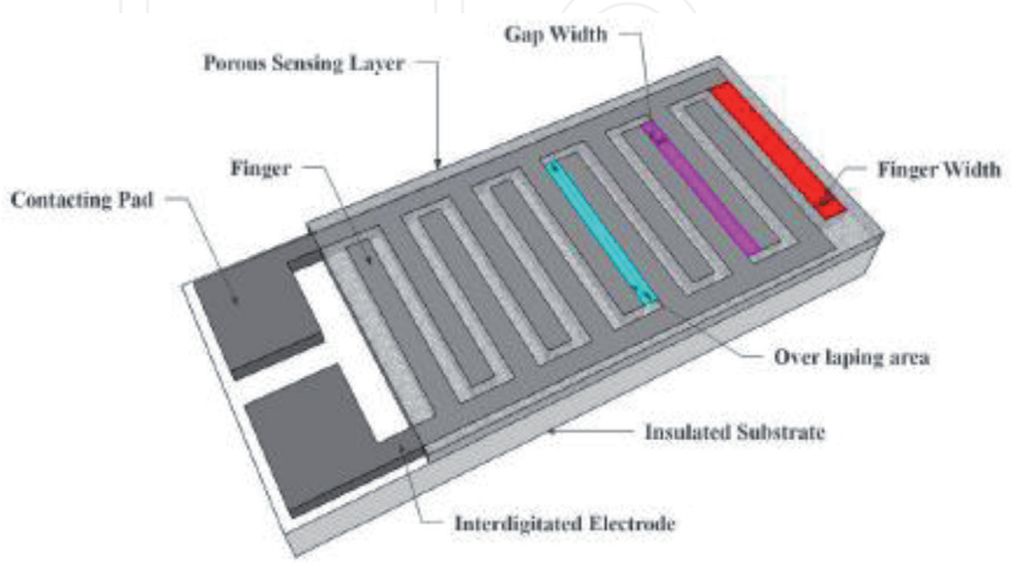

Figure 6.
The above diagram shows the planar thick/thin film based humidity sensor based on interdigital structure with porous sensing element.

3.4 Impedance type humidity sensors

These type of humidity sensors contain noble metal electrodes, which are either deposited on a glass or a ceramic substrate. The techniques of thick film printing and thin film deposition are used for depositing these noble metal electrodes. Interdigital electrodes configuration is most widely used. Thin films for humidity sensing are deposited in between the inter digital electrodes [74–77].

Resistive sensors are based on the measurement of change of humidity levels in terms of change in the electrical impedance of the moisture containing medium. The resistive sensors are based on the principle of adsorption of water molecules and their subsequent dissociation into ionic hydroxyl groups. The response time of these type of sensors is quite small(~10s) [78]. The planar thick/thin film humidity sensor based on interdigital structure is shown in the **Figure 6.**

4. Polymer based resistive humidity sensors

These sensors are based on the thin films of porous polymers [79]. The polymeric films take up water vapour molecules from the atmosphere. These molecules condense in the presence of pores of the capillaries. This water vapour intake produces changes in physical or electrical properties of the polymeric material [80, 81].

A new type of humidity sensors has emerged lately based upon polymer electrolytes, which are also called poly electrolytes. Poly electrolytes are a group of polymers, which have electrolytic groups in them and display conductivity, when they are exposed to water vapour molecules. The poly electrolyes can be classified on the basis of their functional electrolytic groups, into following three major categories [29]:

i. Quaternary ammonium salts

ii. Sulfonate salts

iii. Phosphonium salts

Polyelectrolytes are hydrophilic in nature and tend to dissolve in water [82]. But polyelectrolytes based humidity sensors become non-reliable, if the humidity levels in the surroundings is quite high. In comparison to polyelectrolytes, humidity sensors based on conducting polymers like poly (3,4-ethylenedioxythiophene) (PEDOT) or poly (3.4-ethylenedioxythiophene-poly(styrene-sulfonate) (PEDOT-PSS) show high sensitivity to moisture and are partially hydrophobic [83, 84]. Much work has been done by the research investigators in the recent past, to improve the design of humidity sensors based on polymer electrolytes, to make them water resistant. These methods include grafting, copolymerization, cross links formation, interpenetrating network structures, metal oxide added polymers, photochemical cross linking reactions, anchoring of polymer membranes on the electrode surfaces by means of ultraviolet radiation and addition of dopants [85–88].

The creation of strong conjuctions between polymers and plastic substrates is also a subject of research investigations for the last few years. With the introduction of bonding matrices, prepared by different physical and chemical techniques, this problem has been solved to a considerable extent. Electrospinning method has been used to fabricate composite nanofibres, containing silicon-containing polymer

electrolyte, polyethylene oxide and polyaniline. It was found that the presence of polyaniline (PANI) in the nanofibres led to the decrease of the impedance of the thin films. It was further observed that the adhesion of film to both the substrate and electrode was due to the formation of nanostructure beads in the nanofibres [89, 90]. To increase the conductance change of resistive polymeric humidity sensors based on conjugated polymers, doping agents are used. Poly (p-diethylnylbenzene) (PDEB) has been synthesised with a nickel catalyst in dioxane toluene mixed solvent system at room temperature for humidity sensing applications [91]. Gold nanoparticles are also used in place of Nickel nanoparticles, to increase the conductivity of the thin films. Polyelectrolytes based resistive humidity sensors also suffer from poor conductivity at low humidity levels. This problem is solved by changing the polymer matrix using a superconductor with high conductivity and also mixing techniques.

5. Ceramic based resistive humidity sensors

New humidity detection mechanisms have been developed to resolve the low sensitivity and selectivity problems of humidity sensors. Porous ceramic humidity sensors are fabricated by a variety of techniques such as thick film screen printing, plasma or vapour deposition. In these kind of thick films, the thickness is always kept more than 10 micrometres and dopants are added to increase the dissociation of water molecules. Thin films prepared by vacuum deposition or plasma deposition act as resistive type devices. The released hydroxyl groups change the impedance of thin film elements as they decrease the resistivity of the thin films. For example, $MgCr_2O_4$-TiO_2 material functioned on the basis of physisorption and chemisorption of water molecules followed by protonic conduction [92]. The humidity sensor elements based on these material showed good conductivity at both low as well as higher relative humidity levels. In this type of humidity sensor, heating was necessary to eliminate the hydroxyl groups on the surface and also to remove contaminants like dust, oil and other types of foreign particles. The ceramic humidity sensor is shown in the **Figure 7** [93].

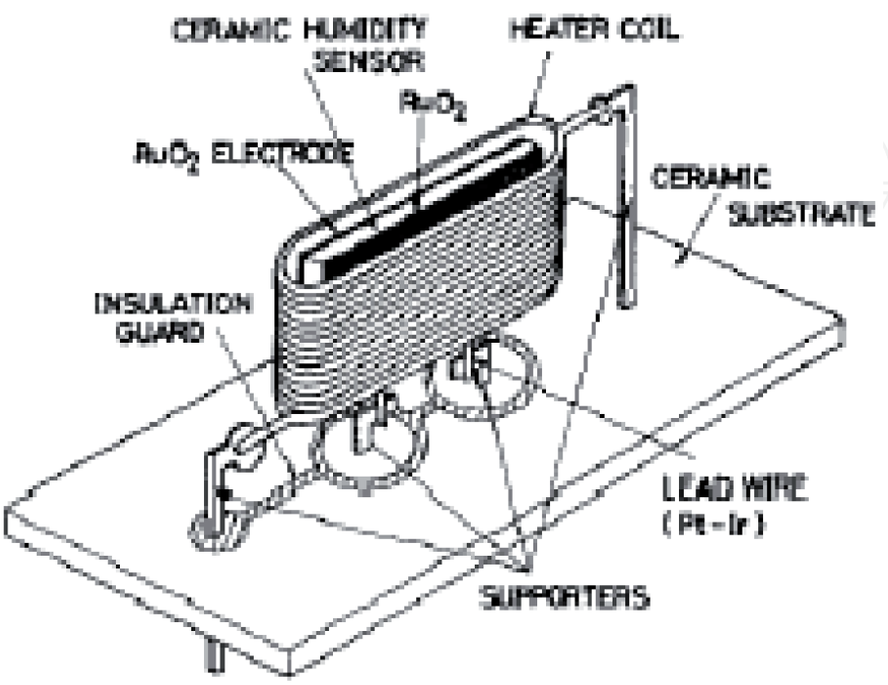

Figure 7.
The above diagram shows a ceramic humidity sensor based on $MgCr_2O_4$-TiO_2.

6. Conclusions/summary

The humidity sensing properties, manufacturing technologies and operating mechanisms of various humidity sensors consisting of different types of materials has been described. Similarly, synthesis and preparation methods for sensors for hygrometric applications have also been explained in this chapter. As protonic conduction type is the most widely accepted mechanism in the majority of humidity sensors, so it is discussed in a detailed manner.

Among all humidity sensor design configurations, the impedance- (resistive) and capacitive-based sensors are the best suited and most popular in the research and industrial environments. Thick and thin film based humidity sensors are also widely used because of cost-effectiveness and ease of fabrication. The humidity sensors based upon ceramic and polymer materials are also used but in lesser magnitude as compared to their above mentioned counterparts and in selected areas of application because of their obvious limitations.

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