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Forty years of adventure with semiconductor gas sensors

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Abstract

This work is to summarise briefly the history of the development of semiconductor gas sensors from the point of view of a researcher working in that field through several decades. Statistical evaluation of publication trends, literature review, device technology and theory of operation are included as well as some recent and earlier results of the author and his colleagues and friends working in the field of semiconductor gas sensors.
The rapid development of material science and semiconductor technology had a strong effect on gas sensor technology in the past. This trend may be extrapolated to the future; the "More than Moore" principle will be valid in the semiconductor gas sensor field too.

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1. Introduction

Semiconductors are very sensitive materials, considering the effects of surface conditions on electrical properties [1]. On the one hand, this fact caused a lot of problems in the earlier phase of semiconductor technology development. The development of surface passivation technology solved almost all difficulties related to environmental effects. On the other hand, the above-mentioned sensitivity resulted in the development of semiconductor gas sensors (SGS). The main motivation of this work is to provide a short summary and development history of the SGS, especially the gas sensitive semiconductor resistors. A large amount of publication has appeared on SGS in the last fifty years (see Table 1). The growth seems to be exponential; however, there is some degree of saturation nowadays. The percentage of results for "SnO_2 gas sensor" compared to "semiconductor gas sensors" is continuously increasing, as well as the absolute number, which does not saturate or decrease (first column in the Table 1). These numbers underline the importance of tin-dioxide in the semiconductor gas sensor technology.

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Table 1. Number of publication using different search expressions

Years	SnO_2 gas sensor/ "SnO_2 gas sensor"	Semiconductor gas sensors/ "Semiconductor gas sensors"	"integrated gas sensor"	"More than Moore"
1960-1964	11/0	842/0	0	0
1965-1969	10/0	1850/0	0	0
1970-1974	30/1	3230/9	0	0
1975-1979	54/3	4550/14	1	0
1980-1984	161/2	6790/54	2	0
1985-1989	272/10	12000/161	9	1
1990-1994	696/33	15700/526	31	0
1995-1999	1680/47	16300/627	58	0
2000-2004	4230/122	51800/1190	142	8
2005-2009	9540/267	66900/1840	218	471
2010-2014	15200/396	64000/2720	225	1910
2011-2015	15800/381	43300/2950	197	2080

2. Scientific background and practical realization of semiconductor gas sensors

The basis for the scientific background of semiconductor gas sensors is provided by semiconductor surface physics (space charge layers, surface states), the theory of surface adsorption/desorption and the theory of catalysis. Adsorption isotherms describe the surface coverage as a function of partial pressure of a given gas component. Adsorbed ions give rise to a work function shift, surface charge or dipole layer resulting in the changing of the space charge in the underlying semiconductor domain.

There are many common features of the SGS construction and development [2-6]: a higher temperature is needed for quick adsorption and desorption (see Fig. 1. as an example), catalytic dopants play a fundamental role in increasing sensitivity and/or selectivity (see Table 2), and the basis for operation is the surface and/or interface potential barrier modulation by the gas adsorption.

Stability is one of the most important requirements against electronic components. Proper surface passivation processes and hermetically sealed encapsulation methods have been developed to build stable semiconductor devices. In the case of semiconductor gas sensors the direction of the development is completely different: the surface should be sensitive to the composition of the surrounding gas atmosphere and special encapsulation is needed in order to exclude disturbing environmental effects, but still enable gas flow or diffusion inside.

SGS devices have been realised as different electric components: diodes [7-9], MOS (metal-oxide-semiconductor) field effect transistors [10], MOS capacitors [11], resistors [3,6,12]. All silicon based SGS devices contain catalytically active metal electrodes. The work function of these metals depends on the environmental gas composition and concentration. The work function has a strong effect on electrical characteristics of the previously mentioned devices resulting in gas sensor function. The bare silicon or metal-silicon interface has got high surface or interface state density around Fermi-level in the forbidden bandgap, thus the work function shift does not affect the space charge layer nearby the surface, because the surface state charge compensates for the work function shift instead of the space charge layer (Fermi-level pinning, quasi isolated surface condition, low surface index). That is the reason why metal-silicon Schottky contacts and silicone resistors are not suitable for gas sensing. Good quality tunnel oxide or gate oxide is necessary to decrease the interface state density, so as to obtain a gas sensitive diode or MOS capacitor/transistor structures. The silicon bandgap is relatively low, thus higher temperature operation is not