RuO_2 and Ru nanoparticles for MISiC-FET gas sensors

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ABSTRACT

Nanotechnology or nanoscience refers to the fact that novel and unique properties of materials are obtained which are due to the small scale. When the particle size reaches nanoscale dimensions, the particle itself could be considered as a surface in three dimensions. For instance, the grain size can affect the conductivity and the resistivity of the material [1].

In this work we have studied catalytically active nanoparticles of RuO_2 and pure Ru as gate material. The particles were synthesized by wet chemical procedure. These materials were chosen because they are conducting and catalytically active. A distinct shift in the depletion area of the capacitance versus voltage curve is observed when measured in oxidizing (synthetic air) and reducing gases (H_2, NH_3, CO and C_3H_6). For RuO_2 particles, the shift is typically ~200 mV for 1% H_2 in synthetic air and ~140 mV for Ru.

Keywords: nanoparticles, Ru, RuO_2, gas sensors, field effect devices, catalytic metal.

1. INTRODUCTION

Metal oxide nanoparticles, having very high surface area and versatile catalytic properties, are promising as gas sensing materials. The metal oxide nanoparticles show interesting behaviors when used as sensing materials for high temperatures (typically at 300 - 400 ^oC). When used as resistive sensing element, oxide nanoparticle layers exhibit high sensitivity (down to ppb level) and enhanced selectivity to the target gas [1].

Metal Insulator Silicon Carbide Field Effect transistor (MISiC-FET) devices are used as gas sensors for reducing gases in harsh environment like engine exhaust and flue gases. By using metal oxide nanoparticles as the gate material of SiC-FET sensors the high surface area and the specific properties of small particles are benefited [2]. A variety of sensing layers may be explored with an intention to enhance the selectivity and long term stability. The gate material in SiC-FETs needs to be conducting and this is even more important for capacitor devices. In case of porous catalytic metals as gate material needed e.g. for detection of ammonia the metal tend to sinter at high operation temperature, which causes drift [3]. By using support in the form of nanoparticles impregnated with catalytic metals, the sintering effect could be reduced.

The excellent properties of silicon carbide (SiC) e.g., wide bandgap, high melting point and chemical inertness make it especially suitable as sensor material for rough and corrosive environments. Metal-insulator-SiC field effect transistor (MISiC-FET) sensors, with buried source, drain and channel region have already been tested with success in several industrial applications [4].

Triple phase boundaries have been proven to be significant for generation of specific gas response e.g. for NH_3 [5]. Use of particles as the gate material increases the occurrence of triple phase boundaries where the catalytic gate material, the insulator and the test gas molecules are in contact. Nano-dimension of the particles has the potential to introduce novel features in sensing parameters like selectivity and speed of response as compared to those for the conventional thin film sensing layers [6].

A number of techniques may be adopted to produce a variety of nanoparticles with unique features for optimizing selectivity, sensitivity and thermal endurance of the gas sensors. Commercially available oxide nanoparticles (e.g. Al_2O_3, SiO_2, TiO_2) might be impregnated with catalytic metals [7]. Aerosol technology [8] can also be used to produce catalytically active particles [9]. Other techniques like flame spray synthesis [10], spray pyrolysis [11] and sol-gel spin coating method [12] have also been used to produce nano-dimension particles with specific gas response properties.

In this work we have tested wet chemical synthesis of catalytically active and electrically conducting particles of RuO_2 and Ru as gate materials in MISiC capacitor devices.

2. EXPERIMENTAL DETAILS

2.1 Gas sensing principle

The sensor mechanism origins from gas molecules, which adsorb and dissociate on the catalytically active surface. The operating temperature together with the material

properties controls the adsorption rate as well as the degree of dissociation. The dissociated hydrogen atoms will diffuse to the metal-insulator interface. There they form a dipole layer, of e.g. OH groups [13] located on the insulator surface [14], which shows up as a voltage shift of the C(V) characteristics of the device, and thereby changes in the surrounding pressure of hydrogen containing gases can be continuously monitored. Some molecules, like ammonia, requires the catalytically active material, the insulator and the gas phase to be present simultaneously. These special sites (triple phase boundaries) can be created by using a porous material or particles. The detection mechanism of the field-effect gas sensors can then be explained in terms of the modulation of an electric field in the underlying insulating layer (SiO_2) due to the specific change in electric charges on the insulator surface. As a result, a shift in the sensor output voltage (sensor signal), is observed. This means that the sensor response characteristics are defined by the properties of both the conducting gate material and the insulator material of the gate. [15].

2.2 Methods for synthesizing RuO_2 and Ru nanoparticles

By using a synthesis method based on NH_3 (25%) precipitate agent, rutile RuO_2 can be produced. The formed amorphous precursor of hydrated ruthenium oxide, "$Ru(OH)_3$", continuously loses water when heated. The crystallization process starts when nearly all the water has been removed from the sample. At various temperatures above 300 °C, crystallization takes place [16]. The rutile RuO_2 nanoparticles were examined by TEM which showed that the particles size are about 20 nm.

In the synthesis of nanocrystalline metallic Ru powder tetraethylene glycol was used as solvent. In the solution $RuCl_3$ (0.20 g) and $C_8H_{18}O_5$, (20 ml) was dissolved and palmitic acid (0.49 g) was added as capping molecule. The suspension was heated to ~40 °C. H_2O_2 (30%) (2 ml) was added slowly and drop wise to the solution which was heated to ~310 °C under O_2-purge. During heating, the solution turned from dark red to dark green. Finally, a black precipitate was obtained, which was separated from the solvent by centrifuging, and later washed twice with deionised water. XRD pattern showed discrete metallic Ru peaks, without the formation of any other crystalline by-products. The average crystallite size was estimated to ~5.0 nm from Scherrer´s equation.

2.3 Fabrication of the sensor device

A schematic of a sensor is shown in Fig. 3, the sensors used in this study were capacitors based on 4H-SiC with a RuO_2 or Ru as the gate material.

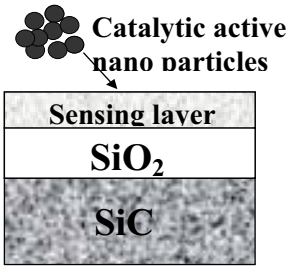

Fig. 3. Schematic picture of a MISiC capacitor sensor.

The total thickness of the insulator was 80 nm and consists of a sandwich structure of SiO_2 and Si_3N_4, this was chosen to improve the device performance. The process started by first growing a thermal oxide of SiO_2 onto the n-doped 4H-SiC surface, followed by a densified layer of Si_3N_4, which also gives a top layer of SiO_x upon oxidation. The SiC is electrically connected via an ohmic backside contact, consisted of alloyed Ni with 50 nm $TaSi_x$ and 400 nm Pt deposited on top (as corrosion protective layer). As bonding pad on top of the sensor a Ti/Pt layer was formed. In this study the active gate materials that are used are RuO_2 and Ru nanoparticles. The active gate region was formed by drop deposition of particles in a suspension of methanol and deionised water using a micropipette. A constant volume (3 μl) of the suspension was taken to define a gate area of ~1 mm diameter for each capacitor. Post-deposition annealing (400 ^oC for 30 min) was performed to enhance the stability of the particles on the SiO_2 surface. This thermal treatment was found also effective for consistent electrical behaviour of the gate material.

The holders were mounted in leak tight aluminium capsules, which are connected to a gas flow line. The gases were primed across the sensor surfaces using a computer-controlled gas mixing system.

The electrical properties were evaluated using a Boonton 7200 capacitor meter and a Hewlett Packard 41924 LF impedance analyzer. The capacitance-voltage (C(V)) characteristics were obtained at 1 MHz. Microstructure of the gate material was characterized by X-ray diffraction (XRD) studies using Philips PW 1729 X-ray generator (40 kV, 40 mA), by transmission electron microscopy (TEM) using Philips EM 400 T, operated at 120 kV using LaB_6 filament and scanning electron microscopy (SEM) using a LEO 1550 FEG microscope.

2.4 Mounting and measurements

A Pt-100 element together with the sensor chip was glued onto a ceramic micro-heater and placed on a 16-pin holder, Fig. 4. The Pt-100 element was used as temperature detector [4], and to withstand temperatures up to 400 ^oC there is an air gap between the holder and the heater. To create electric connections gold bonding are used.

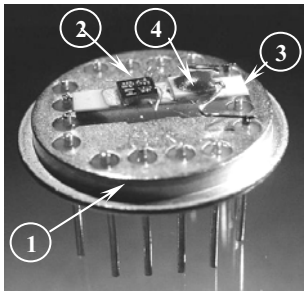

Fig. 4. Mounting of the MISiC capacitor sensors, (1) 16-pin holder, (2) sensor chip, (3) ceramic heater, (4) Pt-100 temperature detector

3. RESULTS AND DISCUSSION

Two kinds of MISiC capacitors, with RuO_2 and Ru as gate materials, were exposed to different gases. The sensors show the same sensitivity pattern but with some small material related differences.

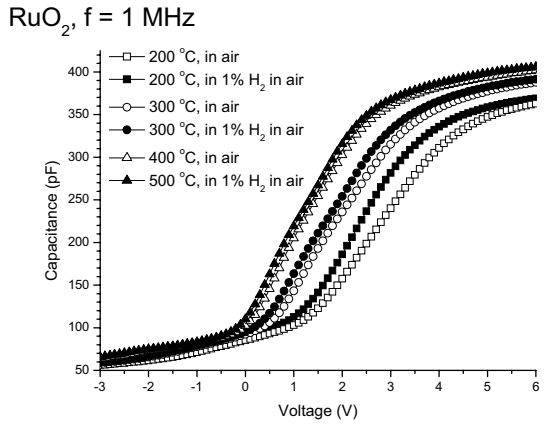

Fig. 5. C(V) curves for RuO_2 capacitor at three temperatures.

The C(V)-curves of the different sensors in different ambients and different temperatures are shown in Figs. 5 and 6. The working point (sensor signal) of the two materials differs in capacitance, for the RuO_2-device ~250 pF is chosen (Fig. 5) and for Ru ~150 pF (Fig. 6). The gate areas in these devices are not well defined due to the deposition method, and this explains the result.

RuO_2 shows the highest response (the voltage shift in the depletion region at a constant capacitance) at 200°C and Ru at 300°C. It seems like RuO_2 nanoparticles has a higher catalytic activity than Ru. The level of the response is however significantly lower for the RuO_2 and Ru materials as compared to porous Pt. This and the lower optimum temperature for the response for RuO_2 as compared to Ru indicate that oxidation and reduction of the material may be involved in the detection mechanism. Comparing the flat band voltages of the C(V)-curves of the two materials it seems like RuO_2 has a somewhat higher work function as compared to Ru. This will be further studied by XPS.

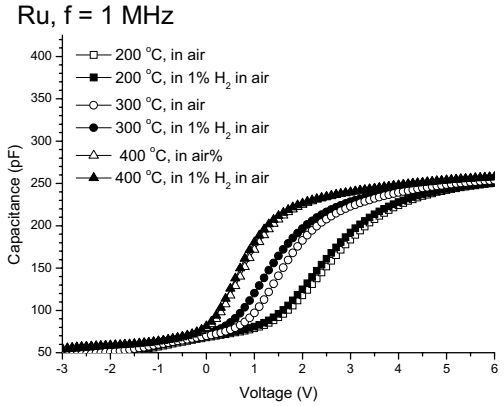

Fig. 6. C(V) curves for Ru capacitor at three temperatures.

The response to typical exhausts and flue gases [17] of the RuO_2 and Ru sensors are compared in Figs. 7 and 8. None of the sensors show any response to CO, while both of them significantly respond to H2, propene and NH3.

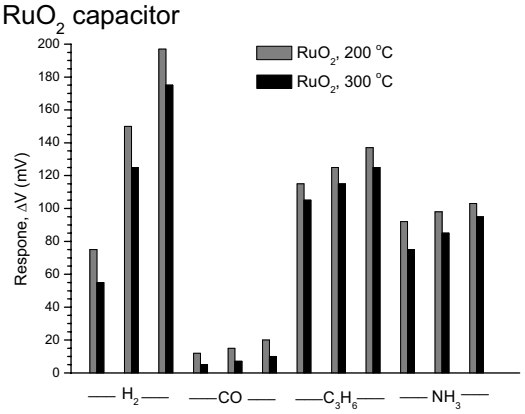

Fig. 7. The gas response for a Ru capacitor (at a constant capacitance) to: 1000, 5000 and 1% H_2, 50, 100, 250 ppm CO, 250, 500 and 1000 ppm C_3H_6 and NH_3 all gases are mixed with synthetic air.

The trend already seen in the C(V)-curves is also shown here, while RuO_2 show the highest response at 200°C, Ru has a higher response at 300°C. This may be used in sensor arrays to get sensors slightly different in selectivity. However, these materials show rather similar behaviour to e.g. sensors with porous Pt gates, which is used as standard sensors today [4]. Non-conducting materials impregnated with catalytic metals, e.g. synthesized by aerosol technology, are expected to give more selective sensors.

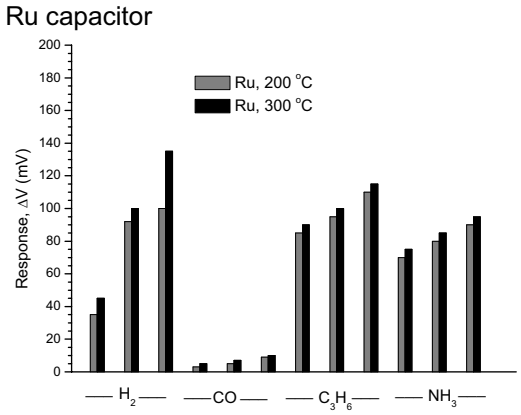

Fig. 8. The gas response for a RuO_2 capacitor (at a constant capacitance), gases as in fig. 7.

4. CONCLUSION

MISiC capacitors with catalytic active nanoparticles as gate material exhibit sensitivity to hydrogen containing gases. The sensitivity pattern depends on the sensing material and the operating temperature of the device. The maximum operating temperature is 300°C for the Ru capacitor and 200°C for RuO_2 capacitor. The sensitivity pattern to reducing gases is similar to Pt-gate field effect sensors, which has the maximum operating temperature at 200°C. There are indications that oxidation and reduction of the Ru / RuO_2 material may be involved in the detection mechanism. This will be further studied by XPS.

Since a wide variety of materials may be used, the metal oxide nanoparticles are potential candidates to be used as gate material for selective field-effect devices.

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