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Structural, optical and electrical characterization of Co-Pd doped TiO_2 semiconducting thin films sputtered on silicon

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The fundamental structural, electrical and optical properties of junction-based devices composed of semiconducting thin films of metal oxide on a semiconductor were examined. Thin films were deposited on silicon and silica substrates by hot target reactive magnetron sputtering process. During the deposition base TiO_2 films were doped with Co, Pd transition metals. Electrical and optical beam induced current (OBIC) analysis confirmed the formation of a junction based on a semiconduting thin film of metal oxide–semiconductor interface.

Keywords: thin film, magnetron sputtering, hot target, oxide semiconductors, heterojunction.

1. Introduction

It has been well known that semiconducting thin films of metal oxides may have interesting optical, chemical and electrical properties [1].

Low conductivity of most metal oxides is the result of a wide forbidden bandgap (over 3 eV) that only extremely few electrons can be excited from valence into conduction band. Electrical conductivity of oxides rapidly increases with an increase of temperature and is proportional to concentration of defects. This would enable one to manufacture high-power and high-temperature electronics based on metal oxides.

Studies of the electrical properties of semiconducting metal oxides [2] have shown that oxides can display native *n* or *p*-type conductivity. Conversion from *p* to *n*-type or *vice versa* by simply introducing aliovalent donor or acceptor ions into a master lattice is difficult and rather limited. The manufacture of semiconducting *p* and *n*-type thin films could open up the possibility of developing a large variety of junction-based

devices [2]. In the past few years some authors [3]–[5] have proven that introducing ions of transition metals into TiO_2 lattice may modify its optical and electrical properties.

For the purpose of the present work thin films of semiconducting metal oxide based on TiO_2 lattice were deposited on silicon substrate in order to form a junction. TiO_2 host matrix has been chosen because of its good mechanical resistance and good stability. Thin films were manufactured using a low pressure hot target magnetron sputtering process [6]. Films were doped during deposition by other transition metals such as Co and Pd ones.

The structural properties of manufactured films were examined by X-ray diffraction (XRD) technique and amorphous behaviour as well as nanocrystalline grains were found.

I-V and *C-V* measurements showed that between the thin film of metal oxide and silicon used as a substrate an electrical junction was formed.

Optical beam induced current (OBIC) analysis showed that two opposite junctions were formed at the metal–metal oxide film and metal oxide–semiconductor interfaces.

2. Experimental procedure

For deposition of thin films of metal oxides, numerous techniques (*i.e.*, sol-gel, physical vapor deposition, magnetron sputtering, *etc.*) have been applied [7]–[10]. In the present work, the low pressure hot target reactive magnetron sputtering process has been used [11].

Thin films were sputtered in the vacuum chamber pumped with diffusion and rotary pumps to the pressure of 8×10^{-4} Pa. A circular magnetron with 100 mm diameter and 3 mm thick titanium (purity 99.99%) disc was used. The Ti target was placed at a distance of 1.5 mm from the cooling plane. The magnetron was supplied by pulsed power in the unipolar mode with 165 kHz sinusoidal pulses. The distance between the target and the substrate was 90 mm and the temperature of substrate during deposition was about 570 K. The titanium target was sputtered in reactive atmosphere using oxygen gas of high purity (99.999%). Stable oxygen plasma has been obtained by choosing proper reactive gas pressure (about 10^{-1} Pa) and appropriate level of active power. The power released in plasma enabled the heating of the target to about 873–973 K. Owing to additional target oxidation, metal oxide molecules can be formed and sputtered directly from the target. That makes the sputtering process more efficient and the deposited thin films are homogenous with the grain sizes in the range of nanometer.

As the dopants Pd and Co sheets have been co-sputtered from Ti target in order to make Ti-Co-Pd oxide composition. Co and Pd dopants have been estimated to be of 15.8 at.% and 6.9 at.%, respectively, in the whole atoms raising from the mosaic target of material from the target.

Samples were deposited on highly doped (10^{-4} Ωm) *p*-type <100> oriented silicon wafers and on amorphous SiO_2 substrates. In order to make electrical measurements

Ti_{10}-W_{90}-Ag metal contacts were evaporated through the mask onto the metal oxide film and on the backside of silicon wafer.

The thickness of the films obtained, measured by optical interference method with Hg (551 nm) filtered lamp was about 500 nm.

3. Results and discussion

3.1. Structure

X-ray diffraction (XRD) examinations were performed on a DRON-2 powder diffractometer using Fe-filtered Kα Co radiation. XRD pattern (Fig. 1) of deposited sample shows amorphous structure of the film obtained. The post deposition annealing process for four hours at 1070 K in the air resulted in the formation of a rutile phase of titanium dioxide. Also, palladium oxide and metallic phases of palladium have been

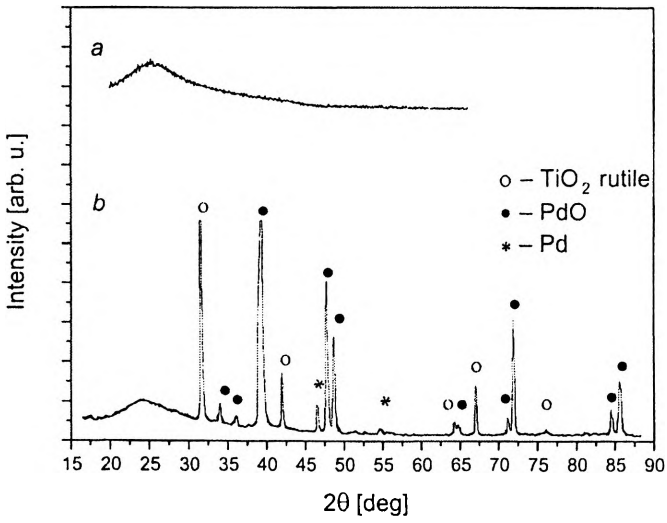

Fig. 1. X-ray diffraction patterns of the Ti-Co-Pd oxide for: deposited (*a*) and annealed sample (*b*). Symbols indicate diffraction peaks corresponding to the identified phases.

found in the sample. After the run involving the crystalline form inversion the sample was cooled down together with the furnace to room temperature, in order to determine the crystallite size from Scherrer equation corrected for instrumental and spectral line broadening and $K\alpha_1\alpha_2$ doublet [12]. The average size of crystallites was about 40 nm, which indicates a high quality nanocrystalline character of the manufactured film.

3.2. Electrical properties

The resistivity of the thin film obtained, measured at room temperature using a four -point probe, was 30×10^{-2} Ωm for deposited samples. The annealing process results

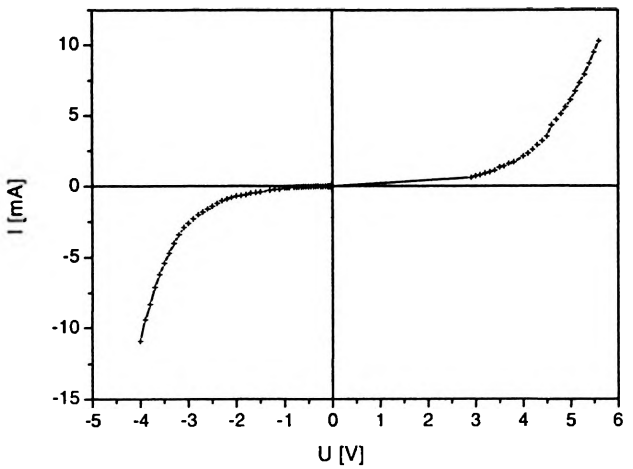

Fig. 2. Current-voltage characteristics of thin film of Ti-Co-Pd oxide deposited on *p*-type silicon wafer.

in an increase of resistivity by about two orders of magnitude due to crystalline phases formation in the film.

In order to examine the basic electrical properties current-voltage (*I-V*) characteristics (Fig. 2) have been determined and capacitance-voltage (*C-V*) measurements (Fig. 3) performed.

The *I-V* characteristics (Fig. 2) were similar to those observed in the case of varistors [13]. For varistors, interfaces existing between grains result in formation of so-called back-to-back or double Schottky junction. The electric charge transport in such materials is affected by grain boundaries which reduce conductivity of the whole structure. The sample under examination was similar to the well-known metal–insulator–semiconductor (MIS) structures, but in our case instead of an insulating film a semiconducting thin film was used.

Characteristics presented in Fig. 2 suggest that two opposite junctions could be formed. The first junction was created at the interface consisting of metal (gate) and thin metal oxide film. The second one was formed between the oxide film and base semiconductor.

The *C-V* measurement (Fig. 3) was carried out at room temperature using the DLS-82E spectrometer with a sine wave of 100 mV rms amplitude at a frequency of 1 MHz. These characteristics exhibit large variation of capacitance with applied voltage. Similar to *I-V* measurement, the center of *C-V* characteristics was shifted towards positive bias. As the voltage gate was applied, the semiconductor–oxide interface was depleted, which resulted in the formation of space charge region (scr). However, not only the substrate was depleted. As the oxide was doped, the electric charge existed in the film and scr could also be present near the gate. When the applied voltage was swept between positive and negative magnitudes a hysteresis loop was observed. The presence of the hysteresis loop could be the result of electron-hole injection from the gate or from the semiconductor to oxide and of a

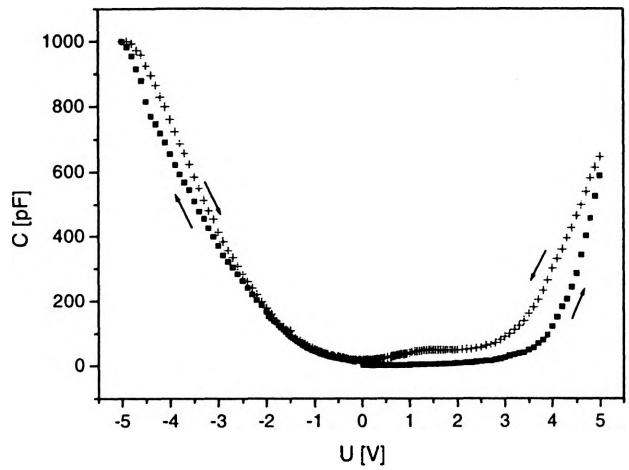

Fig. 3. Capacitance to voltage characteristics of thin film of Ti-Co-Pd oxide deposited on *p*-type silicon wafer. Arrows show the direction of dc bias polarization.

mobile charge existence in the thin film. Another possible reason is the presence of ferroelectric behaviour of manufactured film since Co ions were used as a dopant in TiO_2 lattice [14], [15].

3.3. Optical properties

First, in order to study the basic optical behavior of a thin film of Ti-Co-Pd oxide, optical transmission measurements have been curried out (Fig. 4).

The fringes observed in the transmittance spectra were due to the interference between two optical interfaces: air–thin film and thin film–substrate (SiO_2). The cut-off wavelength of the transmission curve occurs at about 573 nm. The transmission

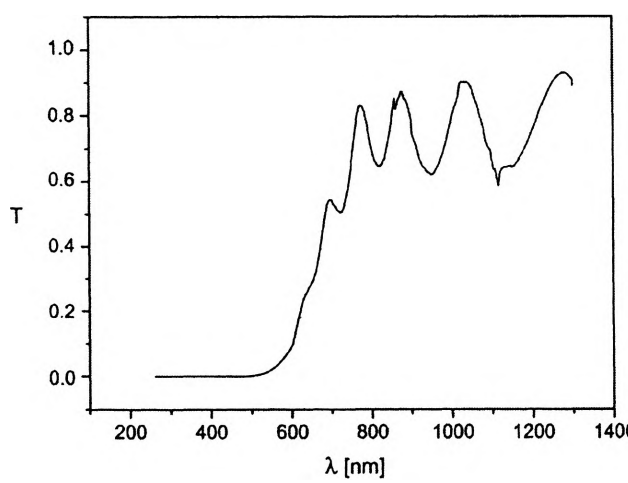

Fig. 4. Optical transmission spectra of analyzed thin film of Ti-Co-Pd oxide.

results show that incorporation of Pd and Co dopants into TiO_2 lattice results in a shift of the absorption edge towards the longer wavelength region. Near the absorption edge the optical bandgap energy E_g^{opt} has been estimated to be of 2.16 eV. Therefore, the main optical bandgap energy of TiO_2 reported in literature to be of 3.0–3.2 eV [16] decreases to the estimated value for the deposited Ti-Co-Pd metal oxide film.

In order to study the metal oxide–semiconductor interface, the OBIC analysis has been applied. In Figure 5**a**, photocurrent spectra *vs.* light beam position "in-line" on the *p*-type silicon covered by Ti-Co-Pd oxide film has been presented. The characteristics were measured at three different wavelengths of incident light. A schematic diagram of the analyzed structure has been shown, too (Fig. 5**b**).

On the basis of transmittance measurements two well transmitted wavelengths through the film of 730 nm and 1000 nm were chosen in order to facilitate generation of the electron–hole pairs at the metal oxide–semiconductor interface. Additionally, one wavelength of 380 nm was selected in the range of high oxide absorption and was not transmitted.

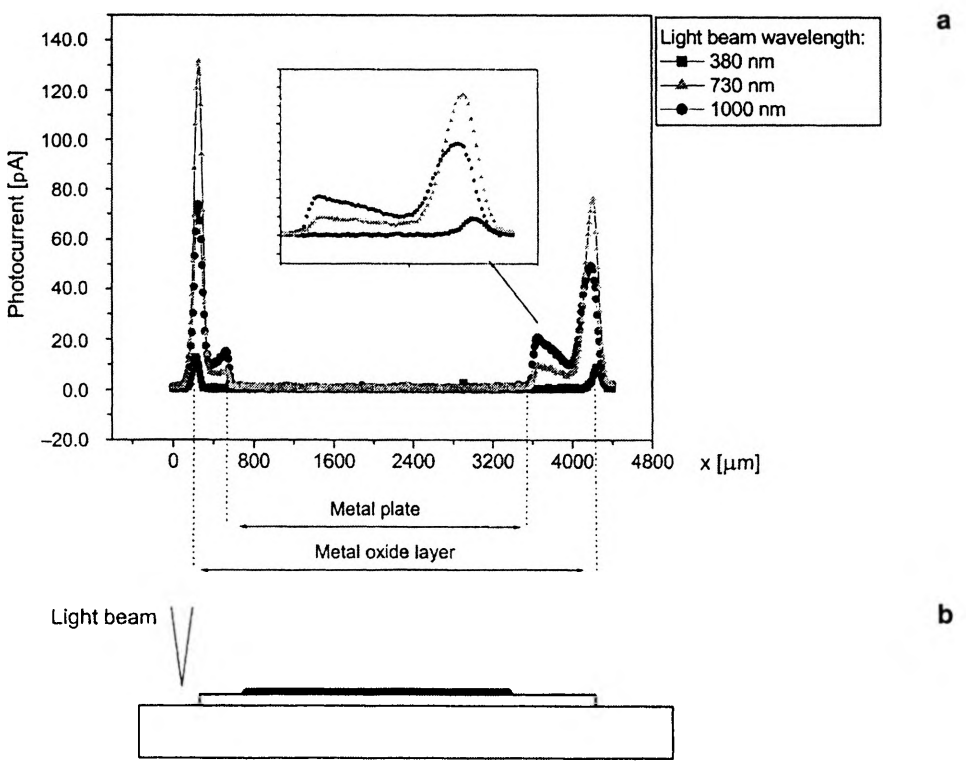

Fig. 5. OBIC analysis: **a** – photocurrent spectra *vs.* light beam position on the *p*-type silicon covered by Ti-Co-Pd oxide film, **b** – a schematic diagram of the device under test. The measurement was carried out at three different wavelengths of the light used (without any correction of the power of incident light).

In Figure 5, an increase of measured current was observed, which indicates the presence of the scr near the two formed junctions. Electrons and holes generated near the interfaces are separated by built-in potential of the junctions causing the rise in the amplitude of measured photocurrent. The higher peak of induced current at the perpendicular metal oxide–semiconductor junction is due to higher absorption and higher efficiency of photon to electron energy conversion in silicon than at the metal oxide–semiconductor or metal oxide–metal interface. Also, the power of incident light could be due to thin film absorbance, light scattering from the surfaces and interferences at the optical interfaces between air–thin film surface and thin film–substrate. Another possible reason is deeper depletion of the scr.

Using different wavelengths in the experiment allows us to indicate the optically active regions which were equal to physical dimensions of analyzed structure. On the basis of the line scans presented in Fig. 5, due to the variation of amplitude of induced current, it is possible to localize the electrically active areas. In this case, both scrs formed near the two manufactured junctions were located in the thin metal oxide film. Poor penetration of space charge into the semiconductor substrate could be explained by low resistivity (*i.e.*, high dopant concentration) of silicon used. This can be considered as a good conductive contact.

4. Conclusions

The *C-V* measurement shows that in Ti-Co-Pd oxide films, consisting of a large number of nanocrystalline grains, the space charge region may cover a large fraction or even the full volume of film. Electron and hole traps found at the interfaces, *i.e.*, at grain boundaries, serve the depletion or even inversion of the electric charge of adjacent grains and corresponding space charge barrier is created. If sufficiently high voltages are reached, a high current may flow through the structure in both directions.

Transition metal ions introduced into the TiO_2 lattice result in a decrease of its main optical bandgap due to the dopant incorporation. High defect concentration and the local charged spaces at grain boundaries led to the formation of quantized energy levels, so-called localized energy states introduced in the forbidden bandgap of the metal oxide semiconductor. Thus, the electron charge transport through nanocrystalline film is due to electron or hole tunnelling which may be excited and hop from one localized energy site to another.

Results obtained by OBIC method allowed us to localize two scrs which were formed at the interface of metal–oxide and oxide–semiconductor, creating two back-to-back junctions. This fact can be observed in *I-V* characteristics and photocurrent spectra *vs.* light beam position.

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