Structural Characteristics of Plasma-Induced Bonded Cobalt Oxide Films on Silicon Substrate

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Abstract

In this work, the characteristics of the Co_3O_4-Si structure produced by plasma-induced bonding technique were studied. The produced structure was an asymmetric heterojunction consisting of n-type Co_3O_4 on a p-type silicon substrate. The Si substrate and Co_3O_4 sample were bonded by subjecting them to the plasma formed between two electrodes. The main measurements included the structural characteristics of the formed structures. The results explained better characteristics than those of the same heterojunction produced by thermal evaporation technique.

Keywords: Plasma–material interactions; Electronic transport; Heterojunctions; Bonding
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1. Introduction

Although the main driving force for development of bonding has been production of silicon-on-insulator (SOI), several other high potential applications of bonding have emerged in microelectromechanical systems (MEMS) and as a way of integrating dissimilar crystalline materials. To reach a sufficient level of maturity, bonding procedures need to be optimized and standardized according to the application. Also, bonding requires a high-temperature annealing step after the room temperature joining, to ensure the formation of a strong and uniform bonding. This high temperature annealing is sometimes incompatible with many applications and it may cause material degradation, especially when bonding thermally mismatched materials. Back to the pioneering days, low temperature bonding procedures have been highly desirable. Figure (1) shows the principle of plasma-induced bonding technique.

If two solids with clean and flat surfaces are brought into close proximity at room temperature, attractive forces pulls the two bodies together into intimate contact so that bonds can form across the interface. The phenomenon was given rather little attention until in the last decades when semiconductors bonding found several applications in mircomechanics, microelectronics and optoelectronics.

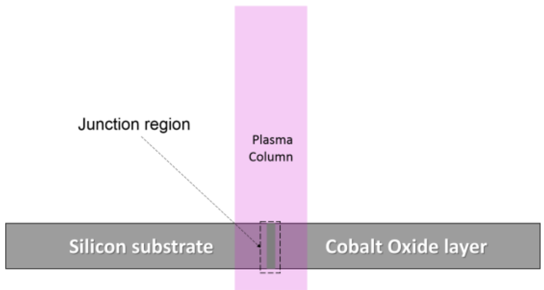

Fig. (1) The principle of plasma-induced bonding technique

Chemically reactive plasma discharges are widely used to modify the surface properties. The relative importance of a specific discharge depends on input power, gases, reactor volume and geometry, gas flows, etc. For instance, plasma discharges are employed for etching, deposition or surface cleaning. The gas-chemistry and the plasma parameters (effect, applied voltage, pressure, plasma density, etc.) that are being used govern the plasma/surface interactions. A variety of gases are such as Ar, O_2, SF_6, Cl_2 and CHF_3 are used for this purpose.

The freedom to integrate diverse materials is one of the advantageous features of the bonding technique. In design, no consideration has to be taken to use lattice-matched materials. Several high-potential applications are reported using dissimilar materials integration by bonding. Fabrication of semiconductor lasers directly on Si substrates have also been achieved using wafer bonding [13].

In this work, the use of plasma activation of the surfaces before bonding has been examined to achieve a low-temperature bonding.

2. Experimental Part

High purity (99.99) (100)-oriented p-type silicon wafers of 500μm thickness and 3Ω.cm resistivity were used in this work. Also, high purity (99.99) cobalt oxide (Co_3O_4) was used to form 350μm-thick samples. Both samples, Si and Co_3O_4, were washed with distilled water then rinsed in ethanol and subjected to ultrasonic waves for 10 minutes, then dried by hot air. The silicon samples were then cleaned with HF for 5 minutes to remove any residual oxides which have existed on their surfaces. Both samples were softly grinded and polished to obtain flat surfaces. Then, these samples were rinsed in ethanol to remove acids then dried to be ready for processing.

The Si and Co_3O_4 samples were mounted inside the plasma system, which is working under vacuum of 10^{-6} mbar at room temperature. The silicon substrate was mounted on a holder made of stainless steel at a specified distance from the anode and the Co_3O_4 sample was placed on the Si substrate. The samples were placed at a position that the plasma is entirely surrounding the sample. Discharge voltage and current are 15 kV_{DC} and 3 A, respectively. Argon gas at a pressure of 1 mbar was used to generate the discharge plasma. The sample was maintained inside the operated system for 10 minutes before being removed and tested.

Before bonding, the native oxide is removed from the surfaces to have a solid-to-solid bonding [14-15]. However, the bonding is very weak at room temperature and after low-temperature annealing because of the hydrogen-terminated surface. A high-temperature annealing above 520°C is necessary to desorb hydrogen from surface and enable a covalent bonding.

The difference in thermal expansion between Co_3O_4 and Si will induce high mechanical stress in the material when annealing the bonded samples at high-temperatures. The thermal stress degrades the material by generating defects. It can also cause cracks and completely debond. The main degradation occurs in Co_3O_4 since Si is a mechanically stronger material.

The samples were subjected heating up to 600°C within 5 minutes then left to return to its initial temperature within the same period of time. Topography of the treated samples was performed using Leitz-Metallux optical microscope at different magnifications (50x, 100x, 150x) while the morphology was introduced by the field-emission electron microscopy (FE-SEM) using an Inspect F50 instrument.

In this work, Co_3O_4/Si samples were prepared to introduce the repeatability of this technique. Along eight days, a sample was daily prepared and processed at the same conditions. As will be shown later, the presented results are the average of the best five samples those seemed identical to each other. Therefore, this technique has very good repeatability as the preparation and processing conditions are kept stable as possible. The experimental preparation and processing conditions mentioned above can be considered as the optimum to obtain the best results in this work. These results were compared to the data available in the literature as well as the results obtained by several local works.

3. Results and Discussion

If two identical solids with the same orientation are bonded together without misalignment and without interface contamination, they should merge into one. However, there are always deviations from the ideal case. In the bonding technique, there is always an unavoidable misalignment between the bonded solids and therefore misfit dislocations appear. Misfit dislocations will also appear at the bonded interface if two solids of different orientation or different lattices are bonded. The presence of native oxides, adsorbed surface contaminants and interface bubbles (voids), also inhibit a perfect solid-to-solid transition region. Figure (2) shows the FE-SEM of the Co_3O_4 layer bonded to the silicon surface in this work, while figure (3) explains the structure of the bonded samples where the misfit in the Co_3O_4-Si interface is shown.

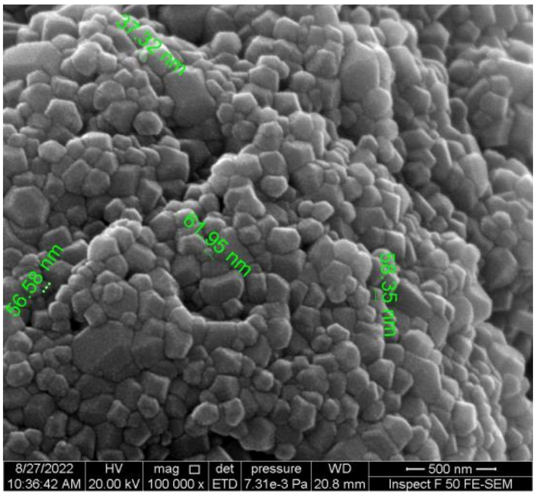

Fig. (2) FE-SEM image of Co_3O_4 layer bonded to Si surface

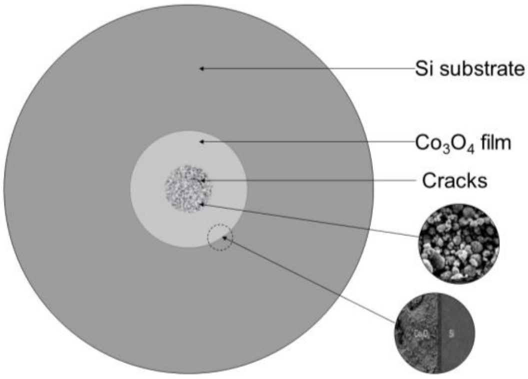

Fig. (3) Structure of the bonded samples where the misfit in the Co_3O_4-Si interface is shown

Defect-etching techniques were found to be more suited for investigations of bulk material defect introduced by the bonding technique, arising mainly from thermal mismatch stress. Defect-etching uses etch selectivity to reveal crystal imperfection such as dislocation. The dislocation appears as pits on Co_3O_4 surface and their origin is traced from the shape of the pits, as shown in Fig. (1). The defect-etching is easy, quick and a more direct approach than electron microscopy. It allows investigations of large areas and in combination with chemical thinning, it was possible to map the dislocation density throughout a bulk. For Si and other semiconductors, defect-etching techniques are well developed and frequently used.

Integration of Co_3O_4 and Si has attracted much interest since the unique properties in each material can be combined in devices or systems, such as Co_3O_4-based magneto-optic and magneto-electric devices and optoelectronics components.

The epitaxial growth of Co_3O_4 on Si substrate is hampered by the difference between the lattice constants of the materials. However, using bonding for the integration, the lattice-mismatch becomes no obstacle. Unfortunately, there is a large difference in thermal expansion between Co_3O_4 and Si. When bonding solids of dissimilar materials and annealing at elevated temperatures, the thermal mismatch will induce high thermal stress in the material.

4. Conclusions

A Co_3O_4-Si heterojunction was produced by plasma-induced bonding techniques. The structural characteristics explained the good bonding interface between the Co_3O_4 and Si samples. Electrical measurements showed reasonable enhancement in the heterojunction characteristics compared to that produced by another techniques. Despite the complexity imposed by the plasma processing system, production of heterojunctions with such enhanced characteristics has advantages of low cost and large size devices.

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