Study of GaAs oxidation in the low-current Townsend discharge

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Abstract. An anodic oxidation of GaAs substrates in a non-self-sustained low-current \textit{dc} Townsend discharge is investigated. The process is carried out at the room temperature in a three-electrode microreactor filled by 98\%Ar + 2\%O\textsubscript{2} gas mixture. Investigation of the oxidation kinetics indicates that the formed oxide is characterized by a high resistivity, \(\rho \sim 10^{11}\Omega\cdot\text{cm}\). It is demonstrated the application of the method for formation of oxide films with dimensions of tens of microns, which thickness is on the nanometer scale. Examination of the “GaAs substrate - oxide layer” interface using the high resolution transmission electron microscopy has revealed that the oxide is characterized by the amorphous structure.

1. Introduction

Formation of dielectric layers on the surface of A3B5 semiconductors is an important technological issue. Different methods to solve it are implemented, which are based on the heat treatment of materials, on wet processes, as well as on the use of plasma-chemical (dry) processes in technology, see for example [1-3]. The last approach is especially attractive because of its potentially high performance in a large-scale production of semiconductor devices and the possibility of achieving results that are difficult to obtain applying other technological methods.

It was demonstrated in [4] an anodic oxidation of single-crystal GaAs in a gas discharge microreactor at the room temperature. A sample of a high-resistivity GaAs being processed served as an anode of a plane-parallel structure operating in the self-sustained direct current (\textit{dc}) Townsend discharge. Such a two-electrode gas-discharge microreactor was filled with nitrogen with a small addition of oxygen. A similar approach was used in [5] for the anodic oxidation of single-crystal InAs at the room temperature. While using a gas mixture of Ar+O\textsubscript{2}+CF\textsubscript{4}, the authors obtained dielectric layers of high quality on the semiconductor surface.

It should be noted, however, that, despite the practical importance of results of [5], using two-electrode microreactors for technological purposes has limitations. These are due to the tendency of a \textit{dc} Townsend self-sustained discharge to transitions to unstable modes, see [6], which is usually unacceptable for a practical use due to the loss of a proper control of the process.

A new design of a gas-discharge plane-parallel microreactor – schematically shown in figure 1 – was used in [7] for oxidation of GaAs wafers. The device consisted of two gas-discharge gaps, (2) and (3), separated by a metal grid (4). In gap (2), a diffuse stable mode of the self-sustained Townsend discharge was provided, which initiated the non-self-sustained discharge in gap (3) – between the grid and a conducting sample (5) being processed, which is the anode to gap (3). The exposure of a sample to the discharge products causes the formation of oxide layer on the semiconductor surface.
Cathode (1) of the device is made of a high-ohmic GaAs wafer, which ensures stability of a spatially homogeneous self-sustained Townsend discharge in gap (2). Its current can be varied in an experiment through excitation of the photo-sensitive cathode by an external source of the IR light. Other details of the experimental setup and its modes of operation can be found in [7].

The present study is devoted to further investigation of properties of oxide films formed at the room temperature on the surface of single crystal GaAs samples using plasma-chemical processing in the microreactor discussed above. The peculiarities of technology that are especially specific for preparation of thin oxide films – the thickness of which are on the nanometer scale – are considered. The resistivity of the oxide film is evaluated when analyzing data on kinetics both of electrical characteristics of the microreactor and the oxide formation. With application of the high resolution transmission electron microscopy it has been found that the oxide structure is amorphous.

![Figure 1. Experimental setup. For the details, see text.](image)

2. Details of the experiments
Parameters of the microreactor schematically presented in figure 1 and used in the current study are as follows. The inter-electrode distances for gaps (2) and (3) are $d_1 = 200$ and $d_2 = 800$ µm, respectively. The mesh electrode has a spatial period of 70 µm. $n$-GaAs (001) samples with electron concentration $n \approx 6 \times 10^{16}$ cm$^{-3}$ have been used as substrates to be oxidized. The main part of experiments is done on plane GaAs wafers subjected to chemical-mechanical polishing. These are referred to as “non-structured” samples.

A possibility of obtaining small-sized dielectric structures on GaAs samples surface directly during the plasma-chemical treatment was also investigated. For this purpose, before a sample oxidation, a dielectric film with holes in it was deposited on a semiconductor surface by the photolithography. When processing such “structured” samples, a non-self-sustained discharge and, accordingly, the plasma-chemical treatment of the GaAs could occur only within the windows opened in the photoresist.

The experiments were carried out with a mixture of gases of 98%Ar + 2%O$_2$ at a pressure $p = 40$ hPa. The samples were processed at the exposure current density $j$ in the range 25–300 µA/cm$^2$. 
The typical area of a sample subjected to the plasma chemical treatment was \(~ 1 \text{ cm}^2\). It was found in the experiments that a decrease in \(j_2\) with time occurred, when the sample was processed at a fixed supply voltage \(U_2\). To provide a constant \(j_2\), the current stabilization mode for the voltage source powering the second gap was set in such experiments. So, an increase in the voltage \(U_2\) was observed in the course of a sample oxidation.

Non-structured samples were applied to study the oxidation process. Parameters of oxide layers were evaluated using spectrally resolved optical ellipsometry and transmission electron microscopy. Ellipsometer “Ellipse 1891” and Philips EM420 and Jeol JEM-2100F microscopes operating in diffraction contrast and high resolution electron microscopy modes were applied to characterize the oxide layers.

3. Experimental results

It was demonstrated in [7] that the oxide thickness \(d_{ox}\) is proportional to the product of exposure current density \(j_2\) by treatment time, \(q = j_2 \cdot t\), i.e. by the Coulomb dose (C/cm\(^2\)). This regularity was found in experiments where the value of \(j_2\) was kept constant during the oxidation of a sample.

Figure 2 shows the \(d_{ox}(q)\) dependence obtained in this work for the experimental conditions described above. The data are obtained by applying the optical spectral ellipsometry (SE) method to determine \(d_{ox}\) values.

Figure 2. Dependence of thickness of the oxide film on the Coulomb dose of a sample exposure. Data are obtained at the fixed current density of the microreactor.

Figure 3. Temporal variation of the microreactor voltage \(U_2\) that supports given current densities of the non-self-sustained discharge in the course of formation of oxide films. To provide proper modes of operation of gap (3), voltage \(U_1\) and resistance of the cathode (1) to the gap (2) were adjusted – see figure 1.

As noted above, at the constant current density of the microreactor, the voltage needed to maintain a non-self-sustained discharge in the gap (3) increases in the course of the oxide formation. To illustrate this feature of the device operation, figure 3 shows the temporal dependence of the voltage difference \(U_2\) on gap (3) – see figure 1 – during the anodic oxidation of samples. The data refer to three values of exposure current density \(j_2\), which are 25, 50, and 100 \(\mu\text{A/cm}^2\). Coulomb doses for all experiments were the same, \(q = 0.2 \text{ C/cm}^2\). The data show that almost identical increase in \(U_2\) relative
to the initial values occurs as a result of exposure of samples at the chosen fixed dose $q$ at different $j_2$. Moreover, at a larger current density, a more rapid increase in $U_2$ is observed.

It is natural to assume that the increase of $U_2$ in the oxidation process is due to the contribution of the resistance of the growing film to the total resistance of the gap (3). The specific resistivity $\rho$ of the oxide can be estimated from the analysis of the kinetics of $U_2$ and the dependence of the layer thickness on the Coulomb dose. It follows from results shown in figures 2, 3 that voltage $U_2$ increases by approximately 20 V, when the film of a thickness of $\sim 20$ nm is formed (which corresponds to the Coulomb dose used to obtained data of figure 3). From this, we obtain the electric field strength in the growing oxide layer $E \sim 10^7$ V/cm. For the current density $j_2 = 100$ $\mu$A/cm$^2$, one obtains resistivity of the oxide film $\rho \sim 10^{11}$ $\Omega \cdot$cm.

![Figure 4. A high-resolution transmission electron microscopy image of the interface "GaAs substrate – oxide layer" of a an oxidized sample. Inserted is the cross-section image of the same sample obtained at a lower spatial resolution. The oxide layer thickness is shown there by arrows.](image)

![Figure 5. An image of a sample oxidized through holes in the dielectric mask deposited on its surface.](image)

Electron microscopy images for a sample prepared at an exposure of 0.14 C/cm$^2$ are shown in figure 4. The data are obtained at different spatial resolution of the method. The images contain the substrate area, an oxide layer, and the layer of a glue that was used in preparing samples to obtain the microscopy data. The periodic crystal structure of the GaAs substrate is clearly resolved in the image obtained at the high resolution. This picture shows that the oxide film is characterized by an amorphous structure. Regarding the composition of the amorphous layer – it can be assumed that a mixture of Ga$_2$O$_3$ and As$_2$O$_3$ oxides is formed under these conditions, similar to the case investigated in [4], where anodic oxidation of GaAs by products of a self-sustained Townsend discharge at room temperature was studied.

Insert in figure 4 shows the cross section data obtained at the lower resolution for the same sample. Diffraction contrast mode of the microscope operation was used to get the image. The oxide layer thickness is near 12 nm and only slightly ($\pm$ 1 nm) varies within the analyzed region. We point out that the direct measurement of the $d_{ox}$ with the TEM is in a good correspondence to the result of
ellipsometry. According to the microscopy data, the oxidation process carried out even at a relatively high current density (which was up to 300 µA/cm$^2$) creates no spatially extended defects in the interface region.

Figure 5 shows an example of a microstructured GaAs surface obtained by the anodic oxidation. Before the oxidation, a dielectric mask with holes was deposited on the sample surface using photolithography. During the oxidation, the voltage of the non-self-sustaining discharge was kept constant. The initial current density in the region of holes in the dielectric mask was $j_2 \approx 100$ µA/cm$^2$. In this experiment, the effective exposure of the semiconductor surface with a discharge was $\approx 0.2$ C/cm$^2$. We stress that the possibility to process a microstructured surface of samples is provided by the high stability of the non-self-sustained Townsend discharge and its almost linear characteristics.

4. Discussion and conclusions
In this work, the anodic oxidation of GaAs by a non-sustained Townsend discharge in argon with an admixture of oxygen was studied. The process was investigated at the room temperature using a three-electrode direct current microreactor.

According to the results of experiments, to maintain the constant value of microreactor current density $j_2$ during a film growth, an increase in the powering voltage $U_2$ is required. The voltage increase is due to the influence of the high resistivity of a growing oxide film on the discharge process in the microreactor gap. We point out that such negative feedback in the oxidation process is quite important in a problem of obtaining nanometer-scale oxide films: The effect tends to suppress non-uniformities in the thickness of a growing film. Indeed, if – due to a fluctuation – the thickness of an oxide in some area becomes less than in neighboring parts, the local current density becomes higher in that region of the sample. This will be accompanied by an increase in the rate of film formation at this place. As a result, a flattening of the surface of the growing oxide will be provided. Such a “self-healing” non-linear effect seems to be especially important at fabrication of quite thin dielectric films, where the presence of non-uniformities may be critical in applications.

The study of the “oxide film - GaAs substrate” interface using the high-resolution transmission electron microscopy reveals that the oxide layer is specified by the amorphous structure. Formation of extended defects in the interface region is not detected by the TEM in the entire range of exposure current density (up to $j = 300$ µA/cm$^2$) applied in experiments.

Resistivity of the oxide layer $\rho$ can be estimated through measuring an increase in voltage $U_2$ observed at the formation of an oxide of a given thickness. It is found that under the experimental conditions of this work, the value of resistivity is about $10^{11}$ Ω·cm for oxide layers of a thickness of $\approx 20$ nm. Thus, the method can be used to prepare thin dielectric films on the surface of GaAs.

Earlier, we found [4] that a film formed at the room temperature at the anodic oxidation of GaAs in a low-current Townsend discharge is a mixture of Ga and As oxides. In this respect, see also [8,9]. Such a process should include diffusion of Ga, As and O atoms in the interface “oxide-GaAs” region. We believe that using elevated temperatures—compared to the conditions of the present work—will increase the rate of film formation and provide obtaining oxide films of an increased thickness.

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