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Transmission electron microscopy investigation of the interface formation between silicon and anodic alumina

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The oxidation of aluminum under anodic bias has been studied for almost 50 years [1]. Due to the nanoscopic size of the relatively regular pore structure it is still a topic of current research and widely used for the fabrication of composite materials. As reported in [2, 3], the self-organized pore growth can be optimized to generate even densely packed, quasi-polycrystalline hexagonal pore structures. These regular structures are then template materials for the preparation of ordered metal nanowire arrays [4–6], carbon based or polymeric nanostructures [7, 8]. In order to obtain the highest ordered structures, high purity aluminum foils have to be pre-treated by annealing and chemical polishing steps [7].

The idea of this investigation is to use films of porous alumina on silicon in chemical and biological sensors with integrated signal evaluation by microelectronic structures on the underlying silicon surface. The task of the porous aluminum is to provide microcavities acting as micro test tubes for chemical substances. Chemical reactions occurring in these test tubes should influence charges into the silicon under the microcavities. Here, the compatibility of aluminum to microelectronic processes and the insulating nature of the oxide are advantageous. The humidity sensitivity, on the other hand, might possibly restrict its applicability to fluid environments, but the realizability of this idea depends mainly on the interface structure between aluminum and silicon, where the charge transport occurs.

This work presents an investigation of the interface between silicon and porous oxide by cross-sectional transmission electron microscopy (TEM) and energy selected imaging (ESI) with a Gatan imaging filter (GIF). These methods give an image of the structure and the chemical composition of the interface.

For the preparation of the porous alumina layer on silicon, a p-doped silicon wafer has been coated with a 2 μm thick aluminum film directly after oxide removal. The wafer was laid on a copper plate and fixed with a teflon ring from the top. The inner ring diameter defines the etching area. The copper plate was then mounted in a cryostat at a temperature of $-1\,^{\circ}$C. The etching solution consisted of a saturated oxalic acid which was enriched with $AlSO_4$. The solution was poured into the teflon ring directly before etching start. The bias was applied between the silicon wafer and a carbon robe in the solution. At the beginning of the oxidation, high current caused a fast heating-up of the substrate which resulted in unstable oxidation conditions. In order to avoid this heating-up, the oxidation was started at constant current with a current density of about 30 mA/cm^2. While the oxide was growing, the related etch voltage continuously increased. The final voltage after 10 min was 36 V. During these 10 min, the voltage continuously increased under current control, while an oxide layer with varying pore distances was formed. While the etch voltage was held constant at 36 V, the sample color was observed. The moment at which the color turned from silver-gray (aluminum) to dark-brown (silicon with oxide), the voltage was switched off. The sample was removed directly after etch stop and rinsed in distilled water. It has to be noted that the current itself is not a measure for the complete oxidation, because a leakage current of up to 10 mA is left after color change.

For the cross-sectional TEM investigations, the samples have been prepared using the Anderson method [9]. The sample was glued with G1 glue from Gatan on a piece of a silicon wafer, sawed in perpendicular direction into mm thick pieces, and mechanically thinned down to a thickness of some μm. Ion milling with a 3 kV argon beam under 6° incident angle and with an oscillating angle of 30° finished the sample to electron transperency.

One interesting result is the minimum aluminum thickness which is needed for the formation of an ordered self-organized porous oxide structure. From [7] it is known that the distance and the diameter of the pores depend on the applied etch voltage. On well defined aluminum substrates the pore distance is almost proportional to the etch voltage (100 V equal 100 nm).

Fig. 1 shows a TEM image of the surface of the porous aluminum film in cross-section. It confirms that the density of the pores decreases continuously during the oxide growth. Unnecessary pores end like tentacles in a certain depth. As expected, the density of the pores correlates with the voltage. Because the voltage approaches approximately exponentially to the end-voltage, the pore density decreases with the same function. At a depth of about 300 nm, the intented pore distance of about 50 nm is attained and the pores grow parallel until they reach the silicon surface. The roughness of the 2 μm thick aluminum film is in the order of 20 nm.

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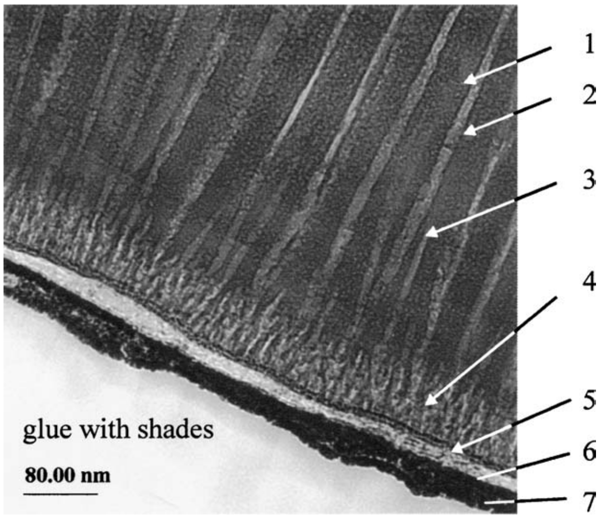

Figure 1 Cross-sectional TEM image of the top-side of the anodically oxidized aluminum film: (1) proceeding pore, (2) aluminum oxide matrix, (3) ending pore tentacle, (4) high density pore structure, (5) original aluminum surface, now: oxide surface, (6) glue G1, (7) sedimentation.

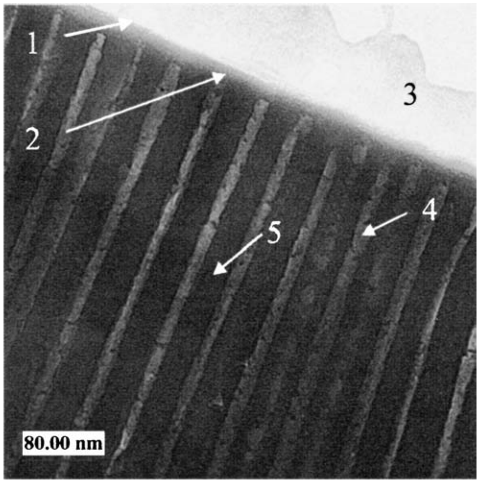

Figure 2 TEM cross-section of the bottom interface between silicon and anodic aluminum: (1) former silicon surface, (2) thin oxide layer, (3) silicon, (4) highly ordered pores, (5) oxide matrix.

The dark line in Fig. 1, which is parallel to the sample surface, consists of polycrystalline copper particles. As known from former investigations on comparable samples, this copper sediment originates from the ion milling. It is always located at the sample edge averted to the incident ion beam. The bright amorphous line between porous aluminum and copper sedimentation is from the remaining glue which assures that the real surface is imaged.

At the bottom side of the porous oxide layer, the TEM image in Fig. 2 has been measured. In order to visualize the cut through the porous structure, Fig. 3 is given. In the central part of Fig. 2, where only one pore row is cut, a constant distance between the pores is observable. In some side location two pore rows at different heights have been cut, and the pore distance seems to halve. Here, the roughness of the interface is given by the flatness of the silicon surface. Due to the higher etch rate, the silicon is much thinner than the oxide and only a thin amorphous silicon layer can be found. The investigation of the material contrast using the Gatan Imaging Filter ascertains that oxygen is present exactly at the edge of the oxide and no remarkable additional oxygen is found at the interface.

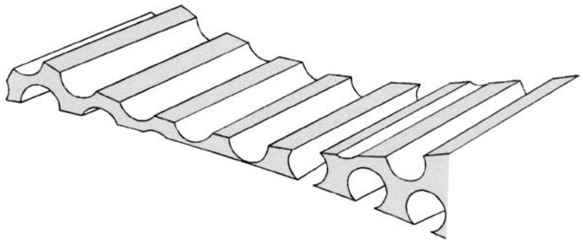

Figure 3 Schematic drawing of the porous aluminum sample prepared for cross-sectional TEM investigation.

From the TEM images and the experimental experience it is concluded that the silicon acts like an etch stop. At the interface, the thin oxide layer as expected in [7] is found and the pore growth stops at a certain distance before the silicon surface. It is known from experiments, where the anodic aluminum has been prepared on aluminum foils and the aluminum has been removed by metal etching, that the remaining nanoporous oxide foils remain permeable for solutions. This experience and especially the non-negligible leakage current after compete oxidation suggest that also the porous aluminum on silicon is permeable for ions.

Such porous inert aluminum oxide layers can also be prepared on prestructured silicon substrates, where the microcavities end above a MOS structure. This MOS structure should be able to detect charges induced by chemical reactions or variations of the optical transmission through the oxide layer.

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