Disappearance Mechanisms of Sub-100 nm Diameter Aluminum Dots on Sapphire during Annealing

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Abstract:
It has been observed by the authors that aluminum nano-dots on single-crystal sapphire substrates will disappear entirely when annealed between 450°C and 1200°C, provided they are ~ 100 nm in diameter or smaller. Such dots have been fabricated at the CNF by electron-beam lithography and liftoff of thermally evaporated metal for a series of annealing experiments to identify the mechanism(s) responsible.

Motivation:
A novel and cost-effective technique for improving the efficiency of compound semiconductor devices built on sapphire substrates has been developed [1] and patented [2] at Lehigh University. This technique requires the fabrication of large arrays of nanoscale “dots” on the substrate in order to improve the quality of the grown semiconductor, leading to substantial gains in final device efficiency. To avoid the hazards inherent in fabricating nanostructures in oxides, we have made use of an annealing process for converting metallic aluminum films on single-crystal epitaxially polished sapphire substrates into sapphire that is epitaxially commensurate with the original substrate [3]. Applied to pre-existing metal nanostructures, the result is the same. Little is known about the behavior of nanoscale aluminum objects under the combined conditions of size scale, temperature range, and chemical environment which are required for the conversion process, as these conditions are extreme as compared to those typical of integrated circuit aluminum conductor structures.

We have regularly observed that during the conversion process, metal dots smaller than a certain threshold diameter (~100 nm) tend to either dramatically deform or disappear entirely during the high-temperature step of 24 hours at 1200°C, yet all dots remain unchanged after the first step of 450°C for 24h. A systematic study of aluminum nanodots annealed in the 450°C to 1300°C range was deemed necessary in order to identify the mechanism responsible for this disappearance and to determine an appropriate technique to prevent such failures in the future. The knowledge obtained in this experiment will also prove instrumental in refining the times and temperatures used in the conversion process, which had been arrived at empirically and originally tailored for use with blanket films as opposed to isolated nanostructures.

Experimental Summary:
The suspected mechanisms for material transport in the relevant temperate range are evaporation, surface diffusion, fracture at the metal/oxide interface leading to wholesale removal of the dot, or extrusion through cracks or flaws in the native oxide shell. It is possible to use the distinct temperature ranges at which each of these mechanisms are expected to be active as a diagnostic tool. In January of 2012, we used the electron-beam lithography capabilities at the CNF to fabricate suitable arrays of aluminum nano-dots for such a study. Dots in the 50-200 nm diameter range were formed by exposure of poly-methymethacrylate on sapphire (JEOL JBX-9300FS) and subsequent deposition and liftoff of 100 nm of thermally evaporated aluminum (CHA thermal evaporator). These dots were then transported to Lehigh University for characterization by scanning electron microscopy (Hitachi 4300 SEM) at normal incidence and 45° tilt, annealing, and re-characterization post-anneal.

At the time of writing, the following conditions have so far been studied: (A) 700°C for one hour, (B) 900°C for one and (C) 12 hours, (D) 1000°C for one hour, and (E) 1200°C for one and (F) 24 hours (six samples total).

Dots of all sizes remain present, even if deformed, for all of the temperatures tested below 1000°C. Complete disappearance of dots has only been observed for diameters less than 70 nm for samples (D) and (E), in dots 80 nm or smaller for sample (F). Spreading (“slumping”) of dots of all sizes is indicated by increased diameter and changed shape at temperatures above 1000°C, and to a smaller degree in sample (C). Slumping in sample (F) is severe, leading to almost complete disappearance of dots up to 100 nm in diameter and nearly 50% increases in diameter. Hillocking...
and extrusion is seen at 900°C and below for dots larger than ~100 nm. Faceting is observed at 1000°C and higher, and is universally hexagonal and commensurate with the c-plane orientation of the substrate.

These results are all in agreement with preliminary observations made in the course of previous work.

**Interpretation of Results:**

The temperature threshold for disappearance at ~1000°C suggests that metal evaporation alone is not the mechanism responsible. The rate of metal evaporation at 900°C [4] would lead to removal of the entire volume of a 100 nm diameter dot in several minutes. Cross-sectional transmission electron microscopy of selected samples will be performed to determine at which point the dots have fully converted to oxide. Further experimentation with annealing temperatures and times and modeling based on these results is ongoing in order to conclusively determine which of the remaining mechanisms are responsible for dot disappearance. Quantitative study of dot spreading rates may also prove useful in separate studies of metal/oxide wetting and/or oxide surface diffusion.

**References:**


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**Figure 1:** SEM of high aspect ratio as-fabricated aluminum dots, ~70-80 nm diameter, at 45° tilt.

**Figure 2:** SEM of dots in Figure 1 annealed at 1200°C for one hour. Dots are spheroidized, but remain present. Smaller diameter dots have disappeared entirely.

**Figure 3:** SEM of as-fabricated aluminum dots, ~130 nm diameter, at 45° tilt.

**Figure 4:** SEM of dots in Figure 3 after 1200°C for one hour, exhibiting slumping and faceting.