Selective CVD deposition of phase change material alloys

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ABSTRACT
Selective Chemical Vapor Deposition of Crystalline Ge-Sb-Te alloys has been accomplished by using Sb and Te precursors which chemisorb but do not decompose on dielectric surfaces in the utilized temperature range. Furthermore, the chemisorbed species prevent the decomposition of the Ge precursor. Therefore, the deposition fills the vias upwards from the metal bottom electrode.

Key words: CVD, GST, selective growth

1. INTRODUCTION

Due to the stringent demands imposed by the scaling roadmap of phase change memory devices, it is becoming increasingly important to understand the Chemical Vapor Deposition (CVD) and Atomic Layer Deposition (ALD) processes options that can be utilized to fill small but high aspect ratio structures with phase change material. Both CVD and ALD methods have provided the means for an increasing number of related studies [1-6]. In the present work, we report CVD growth effected without using any reactive gas or plasma, so that the decomposition selectivity of the precursors utilized allows for growing the material starting at the bottom contact, with no deposition on the dielectric top surface.

2. EXPERIMENTS

The experiment was performed on patterned 200 mm wafers in an Applied Materials chamber, modified for CVD processes, attached to an Endura HP 5500 platform. The deposition was carried out at a chamber pressure of 4 torr, with Ar carrier gas flow ranging from 20 to 60 sccm, depending on the precursor. The ampoules and lines were heated to minimize adsorption during precursors transport. We used TETRAKIS (DIMETHYLAMINO) GERMANE, TRIS (DIMETHYL-AMINO) ANTIMONY and DI-TERT-BUTYLTELLURIDE as precursors. Deposition was effected on wafers which were kept at approximately 300 ^{o}C. The vias were formed either in Si oxide or nitride by a RIE process exposing either TiN or Tungsten as the bottom contact. The vias varied in shape and aspect ratio with the bottom contact diameter ranging from ~ 200 nm to 30 nm, and depth ranging from ~250 nm to 150 nm.

3. RESULTS AND DISCUSSION

Previous experiments related to CVD deposition of phase change materials have shown that the precursors typically used for phase change materials have different rates of incorporation [1,3]. Furthermore, in the absence of a reactive gas, a Ge seed is needed in order to start incorporating Sb and Te. For deposition on blanket wafers this procedure may be successful. However, because the goal of this CVD deposition is to be able to fill 20-30 nm diameter vias with aspect ratios of approximately 3-4, problems will arise due to the influence of the edges at the vias on flow and reactivity. Local accumulation will eventually form a plug which will prevent the material to properly fill the via.

We found a way to overcome this problem by taking advantage of the different reactivity of each precursor with different substrates in order to fill vias. For example, without the use of reactive gases, the utilized germanium precursors tend to decompose on both dielectric and metal surfaces in the temperature range utilized in this study, 250-350 ^{o}C. In contrast, under the same conditions, the Te and Sb precursors do not readily decompose on dielectrics such as Si oxide or Si nitride, while they do tend to decompose on metal surfaces. Furthermore, the above Sb and Te precursors chemisorb on dielectrics as it was determined by x-ray photoemission. These chemisorbed precursors prevent the decomposition of the Germanium precursors on dielectric surfaces, which constitutes the basis for selectivity that this method provides. As for the metallic materials such as titanium nitride (TiN) or tungsten (W), typically used for electrodes for phase change materials, they provide distinct reactivity to the precursors. We found that both Te and Sb precursors readily decompose on W, while the decomposition rate of the used Te precursors on TiN is negligible, as it has been shown before [4].

The selective growth on patterned substrates however, is more complicated due to the different surface mobilities of the precursors on the dielectric surfaces. Therefore, attaining the desired stoichiometry inside the via requires a process that takes into account vapor pressure and surface mobility of the different precursors, as well as bulk inter-diffusion of the different elements. For GST, the bottom electrode material, the CD and depth of the vias each influence the kinetics and uniformity of the growth. This dependence is reflected in the following: a) the chemical interaction of the Sb precursor is stronger on W than on TiN, resulting in faster and more uniform nucleation on the former substrate; b) the precursor arrival rate increases with the feature's CD; c) the growth takes longer to emerge with increasing depth of the via. Once the growth inside the via emerges to the surface, the local flow pattern changes, increasing the capture of precursors and thus the kinetics. Since the nucleation process of the cells are not in phase, the growth on neighbor cells may reach the surface at different times resulting in local screening and thus in some non-uniformity in the final stages of the growth. The latter may be controlled by tailoring the process for each particular surface.

GeTe and Sb2Te3 exhibit similar growth dependence on the via size and bottom material as GST. However, in the case of these binary compounds, the stoichiometry is easier to maintain because these compositions are thermodynamically favored, probably because their crystalline structure is assumed to be determined by resonant bonding [7].

4. SUMMARY

We have demonstrated that selective CVD deposition without using a reactive gas seems to be a viable method to fill up small vias with phase change memory materials, provided that the bottom electrode material used supplies a suitable locus for precursor decomposition.

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Biography

Dr. Alejandro Schrott was born in Buenos Aires, Argentina, where he did his undergraduate studies in Physics. He obtained a Ph.D. in Physics at the University of Washington, Seattle, and then spent 2 years at the Materials Science Department of Cornell University for postdoctoral work. Dr. Schrott has been a Research Staff Member at the IBM T.J.Watson Research center since 1986. At IBM, he has worked on surface and interface properties of materials, in connection with a variety of processes. Dr. Schrott has also worked on processing and characterization and fabrication of exploratory devices based on oxide and organic materials. Presently his work has focused on process development and integration of Phase Change Memory Devices. He is the author of more than 80 publications and 70 issued patents.