Journal of Ceramic Processing Research. Vol. 6, No. 1, pp. 17~19 (2005)

J O U R N A L O F
Ceramic Processing Research

Crystallization and anisotropic dielectric properties of tantalum oxide thin films

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Thin films of tantalum pentoxide, a possible candidate for high-k dielectric gate oxides in integrated circuits, were studied by transmission electron microscopy (TEM). The atomic-layer-deposited material is amorphous, crystallizing into the orthorhombic (L) phase after annealing in the temperature range 750~850 ºC. In situ TEM observations allow the kinetics of the reaction to be established in detail. A combination of TEM and focused ion beam (FIB) techniques was used to determine the capacitance of individual crystallites of known orientation, whereupon it was established that the property differences were less than 10% for orthogonal orientations.

Key words: Crystallization, tantalum oxide, electron microscopy, focused ion beam, anisotropy, dielectric constant.

Introduction

It is now well-recognized that the increasing miniaturization of semiconductor integrated circuits requires the replacement of the major components in field-effect transistors (FET) with advanced materials [1]. In particular silica, the traditional gate oxide, will be superceded by higher dielectric constant (k) metal oxides, such as tantalum oxide, hafnia, zircornia and silicates thereof [2]. One concern with the latter is their lack of stability to crystallization upon annealing or processing, which may well alter their dielectric properties. Furthermore, as the crystal structures are not highly symmetric, there is the possibility that different crystallographic orientations may well have inherently different k values. A basic study of crystallization and its effect on properties is therefore essential to understanding and developing their application. This paper describes an approach to this type of work using in situ transmission electron microscopy (TEM) of tantalum oxide films, with focused ion beam (FIB) microscopy to establish the dielectric properties of individual crystals.

Experimental Procedures

The tantalum oxide thin films used here were grown to approximately 10 nm thickness using atomic layer deposition techniques onto slightly nitrided silicon substrates. Specimens suitable for TEM analysis were prepared by thinning from the back (Si) side, being examined in a Philips CM20 microscope. In situ heating experiments were carried out using standard, well-established procedures (e.g. [3]).

In order to test the dielectric properties, a method was devised to locally deposit platinum electrodes onto individual crystals whose orientation was pre-determined by TEM electron diffraction [4]. This was achieved by breakdown of a suitable organo-metallic gas in a FEI Strata 235 (dual beam) focused ion beam (FIB). Electrical contact was made by the micromanipulator in this machine, with capacitance measured with a HP4284A LCR meter.

Experimental Results

The as-deposited films are amorphous, as confirmed by electron diffraction and high resolution TEM imaging. Annealing in vacuum in an oxygen environment above about 750 °C crystallizes the material, into the orthorhombic L-Ta_2O_5 form [5], again as determined by electron diffraction analysis.

In situ TEM observations and recordings were made at 790 °C, 820 °C and 850 °C to follow the crystallization behavior. In a qualitative sense, it appears to follow a classical nucleation and growth process (e.g. Fig. 1), and plots of the fraction transformed (as determined directly from the images) as a function of time are consistent with an Avrami relationship [6], as shown in Fig. 2. An interesting aspect of the microstructure is the very narrow bend contours in each crystal indicating a significant degree of local distortion. This appearance is very similar to that occurring in the crystallization of some metal silicides, as studied by Smith et al. [7]. However, the temperatures involved here are much higher as we are really extending the range of in situ experiments.

Arrhenius plots of the growth rate of individual crystallites and the time for 30% transformation, as a function of reciprocal absolute temperature, yield acti-

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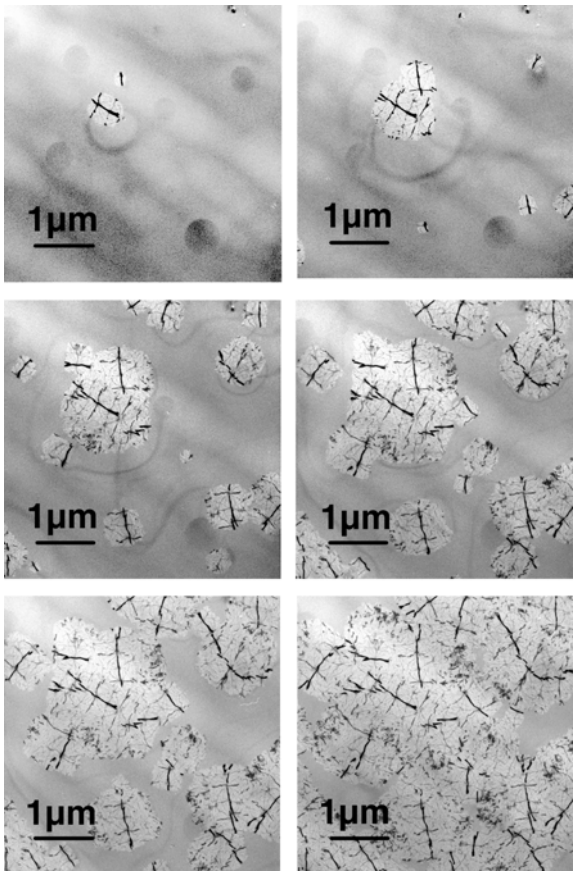

Fig. 1. A series of BF image taken during in-situ heating of Ta_2O_5 film after (a) 9 minutes, (b) 20 minutes, (c) 40 minutes, (d) 60 minutes, (e) 75 minutes, and (f) 130 minutes at 820 °C.

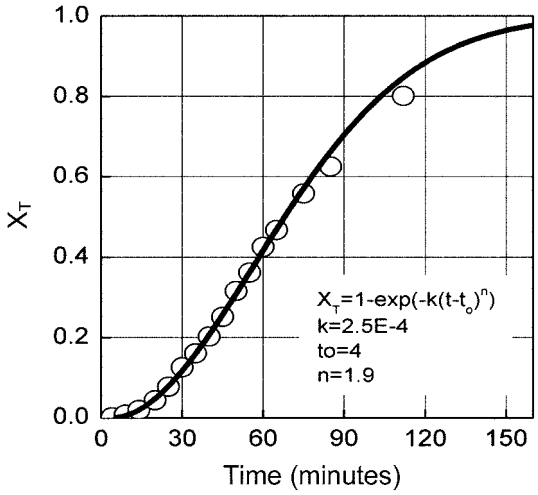

Fig. 2. Avrami plot of Ta_2O_5 crystallization at 820 °C. Crystallization fraction X_T is plotted as a function of annealing time.

vation energies of 4.2 eV and 6.3 eV, respectively [8]. These are noticeably higher than equivalent values for amorphous silicon (2.8 eV, [9]) and for amorphous metal silicides described above (1.1 eV, [7]), which is consistent with reactions which take place in ceramic or oxide-based materials. The grain growth activation

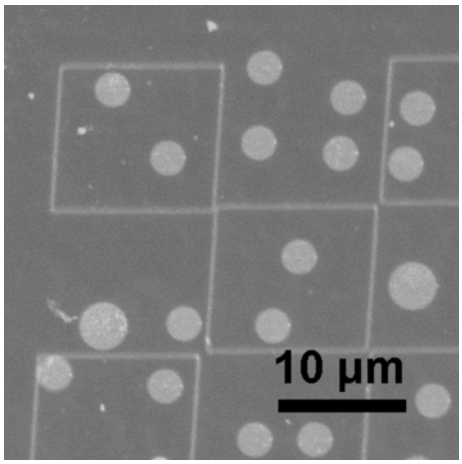

Fig. 3. A SEM image of local Pt deposition using the electron beam in a dual-beam FIB; White circles are the top Pt electrodes, with Pt lines which were used as fiducial markers.

energy for tantalum oxide sintering for instance has been determined to be 5.6 eV [10]. From a processing point-of-view, this implies that the reaction takes place over a very narrow temperature range, below which there is essentially no crystallization and above which there is total transformation.

During detailed characterization of the microstructure it was noticed that the material predominantly crystallizes into two mutually orthogonal orientations, with either [11 1 0] or [0 0 1] perpendicular to the foil surface [4, 8]. From knowledge of the kinetic behavior, individual crystals could be nucleated and subsequently grown to reasonable dimensions such as a few micrometers in diameter. The location of these crystals could be clearly identified by TEM imaging, and these same areas could then be examined in the FIB machine. By careful juxtaposition of the two sets of images, it was then possible to locally deposit a platinum electrode onto each crystal using electron-beam induced breakdown of methylcyclopentadienyl (trimethyl) platinum gas inserted into the FIB chamber [e.g. Fig. 3]. Annealing the deposit to 500 °C, which is well below the crystallization temperature, improves its electrical resistivity to a value suitable for subsequent testing. Determination of the capacitance of each crystallite showed that there were slight differences between the two orientations, which were less than 10%. This is within an acceptable range for processing should for instance either of the orientations exist within an individual FET, which is quite possible considering the shrinking dimensions of the latter (currently 90 nm level).

Summary and Conclusions

This investigation has shown that in situ TEM can be successfully extended to higher temperatures to study the crystallization behavior of oxide or ceramic thin

films (in this case tantalum oxide) which might be useful high-k dielectric materials in the semiconductor industry. Quantitative analysis of recordings of the transformation is consistent with classical Avrami equations, and the activation energies are noticeably higher than those for semiconductor or metallic amorphous-crystalline transitions.

A combination of careful TEM observation and focused-ion-beam examination allows local deposition of Pt electrodes onto individual crystallites whose orientation had been pre-determined. The capacitance of each crystal could then be measured using the omniprobe contact in the FIB. It was found that there was less than 10% difference between orthogonal orientations, and so crystalline anisotropy is not thought to have a significant influence on the practical application of this material in thin-film form. It is worthwhile noting that the complementary capabilities of TEM and FIB are extremely powerful for studies of this type, and we believe this is the first time they have been used this way.

Acknowledgements

This work has been partially funded by the Stanford University Initiative on Nano-scale Material Processing (INMP) and by the Stanford Nano-characterization Laboratory (SNL). Use of facilities in the latter is greatly appreciated.

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