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Full Length Article

Inorganic material profiling using Ar_n^+ cluster: Can we achieve high quality profiles?

T. Conard [a,*], C. Fleischmann [a], R. Havelund [b], A. Franquet [a], C. Poleunis [c], A. Delcorte [c], W. Vandervorst [a,d]

[a] IMEC, MCA, Kapeldreef 75, 3001 Leuven, Belgium
[b] NPL, National Physical Laboratory, Teddington, Middlesex TW11 0LW, United Kingdom
[c] Université catholique de Louvain, BSMA, Croix du Sud, 1 Box L7.04.01, B-1348 Louvain-la-Neuve, Belgium
[d] Instituut voor Kern-en Stralingsfysica, K.U. Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium

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ABSTRACT

Retrieving molecular information by sputtering of organic systems has been concretized in the last years due to the introduction of sputtering by large gas clusters which drastically eliminated the compound degradation during the analysis and has led to strong improvements in depth resolution. Rapidly however, a limitation was observed for heterogeneous systems where inorganic layers or structures needed to be profiled concurrently. As opposed to organic material, erosion of the inorganic layer appears very difficult and prone to many artefacts.

To shed some light on these problems we investigated a simple system consisting of aluminum delta layer(s) buried in a silicon matrix in order to define the most favorable beam conditions for practical analysis. We show that counterintuitive to the small energy/atom used and unlike monoatomic ion sputtering, the information depth obtained with large cluster ions is typically very large (~10 nm) and that this can be caused both by a large roughness development at early stages of the sputtering process and by a large mixing zone. As a consequence, a large deformation of the Al intensity profile is observed. Using sample rotation during profiling significantly improves the depth resolution while sample temperature has no significant effect. The determining parameter for high depth resolution still remains the total energy of the cluster instead of the energy per atom in the cluster.

1. Introduction

While inorganic material sputter depth profiling has been extensively studied and used in the last decades, organic depth profiling has long been beyond reach due to the strong chemical damage produced by the sputtering process. Progress started to be made using cluster ions with one of the first molecular depth profiles published at the end of the 90s by Gillen and Roberson [1] who presented a depth profile of glutamate using SF_5^+. Further improvements were achieved by the introduction of C_{60}^+ [2] as sputter source but it was quickly evidenced that this sputter ion leads to severe limitations for cross-linking polymers [3]. More recently, the introduction of large Ar-cluster beams [4] opened the door to retrieving organic information from about any organic material.

The sputtering by large gas clusters leads to sputter yields that are very strongly dependent on the material properties with factors up to ~1000–10,000 higher sputter yields for organic versus inorganic components [5]. In addition to the slow erosion rates, very poor depth resolution in inorganic matrices is also observed despite the low energy per atom achieved. However, no systematic studies have been published yet on this topic despite the fact that a good understanding is critical to achieve high quality profiles in hybrid systems, where both organic and inorganic components are present.

This work concentrates on the profiling of inorganic materials by large Ar-clusters ions and more specifically on the influence of beam parameters on the sputter induced roughness and depth resolution.

2. Experimental

Within this study on inorganic materials, we focus on Si-based systems as these can be fabricated using standard semiconductor technology with well-known characteristics and high quality. The model system used consists of Al-delta layers embedded in a Si-matrix.

* Corresponding author.
E-mail address: tconard@imec.be (T. Conard).

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Three different structures were investigated. They were prepared on a Si(1 0 0) wafer by growing a thin Al_2O_3 layer by Atomic Layer Deposition (ALD) using a TMAH/H_2O process at 300 °C followed by a Chemical vapor (CVD) deposition of amorphous-Si at 500 °C. The superior growth rate control in ALD allows depositing an Al_2O_3 as thin as 0.1 nm. Structures with one or two single Al delta layers were grown. The single delta layer samples were buried under an amorphous-Si layer of either 10 nm or 20 nm. The structure with two Al-deltas was grown with intermediate 5 nm amorphous-Si and capped with a 5 nm a-Si. Fig. 1 presents the cross-section Transmission Electron Microscope (TEM) and Atomic Force Microscope (AFM) images obtained on the 10 nm-capped single Al-delta sample confirming the nominal layer thickness values and the low surface roughness of the samples. It should be noted that these samples were produced using multi-chamber deposition and that, as a consequence, the Si-surface before deposition of the Al-deltas is slightly oxidized, as it is also observed on the TEM cross-section.

In order to take advantage of different beam configurations, the TOF-SIMS experiments (Time-of-Flight Secondary Ion Mass Spectrometry) were performed on different instruments, all from ION-TOF. Some experiments were performed on a TOF-SIMS IV and others on a TOF-SIMS 5 instrument using a dual beam configuration combining either a 25 or 30 keV Bi_3^+ analysis beam. Three different sputter beams were considered: Ar_n-clusters, Xe or O_2 sputter beam. In all cases, the sputter rate ratio between the analysis beam and the sputter beam was maintained below 2E−3, except for the 5 keV Ar_{2800}^+ sputter beam where a ratio of only ∼1E−2 was achieved. All experiments were performed with the sputter beam impacting the sample at 45 deg. It is not expected that the difference in the analysis beam energy has an impact on the obtained results.

The depth calibration was performed by crater depth measurements using a Wyko NT3300 Veeco optical profilometer. Optical profilometer measurements precision do suffer from the presence of surface oxide. For the Xe and Ar-clusters craters, the error arises from the presence of native oxide, which is similar at the sample surface and inside the crater. The error on the crater depth is thus estimated to 1–2 nm. For the O2 profile, the error is larger due to the presence of sputter induced oxide layer formation and is estimated to max 4–5 nm. Depth scales were established assuming a constant erosion rate.

AFM measurements have been done on an Icon PT coupled with a Nanoscope V controller (Bruker) in tapping mode using AC160TS probes. AFM measurements were performed twice on each sample at a 2 × 2 μm^2 and a 1 × 1 μm^2 area. Both RMS and R_a values of the two areal measurements showed in general variations of less than 5%.

3. Results and discussion

Fig. 2 presents the positive ion depth profiles of the single Al-delta layer (10 nm deep) using 350 eV O_2^+ (blue curve), 350 eV Xe^+ (black curve) or 10 keV Ar_{2800}^+ (red curve) sputter ion beam. Several characteristics can be directly observed: First, on the upslopes of the Al-profiles measured with the Xe and O_2 beams the Al signal does not present a pure exponential increase of the intensity, as would be expected for a pure delta layer. This feature is considered to be characteristic to the sample, arising from updiffusion of Al during the growth of the amorphous Si layer. The best depth resolution (trailing edge) is obtained using the 350 eV Xe^+ beam (decay length (λ) = 2.2 nm/decade), followed by the O_2 induced profile (λ = 2.8 nm/decade). The Ar_n^+ profile leads to an extremely poor depth resolution (λ = 26.8 nm/decade). A second important characteristic is that the maximum of the Al intensity for the Ar_n^+ profiles occurs at an apparent depth of ∼2 nm, compared to the effective depth of 10.0 nm. It should be noted that a small depth-shift of the Al maximum intensity is also observed for the O_2 profile and a larger one (∼2 nm) for the Xe profile. For the latter two cases, this has primarily been attributed to the non-constant erosion rate in the transient region [6,7] and the effect of ion beam induced relocation and is shown to scale with the energy of the primary sputter beam. The results of the Ar-cluster profiles may thus indicate that in that respect the high E value is the dominant parameter and not a low energy per atom (E/n).

Next to the depth profiles, Fig. 2 also presents the roughness of the crater bottom as measured by AFM. The smoothest crater is obtained for the Xe sputtering (R_q = 0.08 nm) followed by the O_2 crater (R_q = 0.16 nm). The Ar-cluster crater is extremely rough

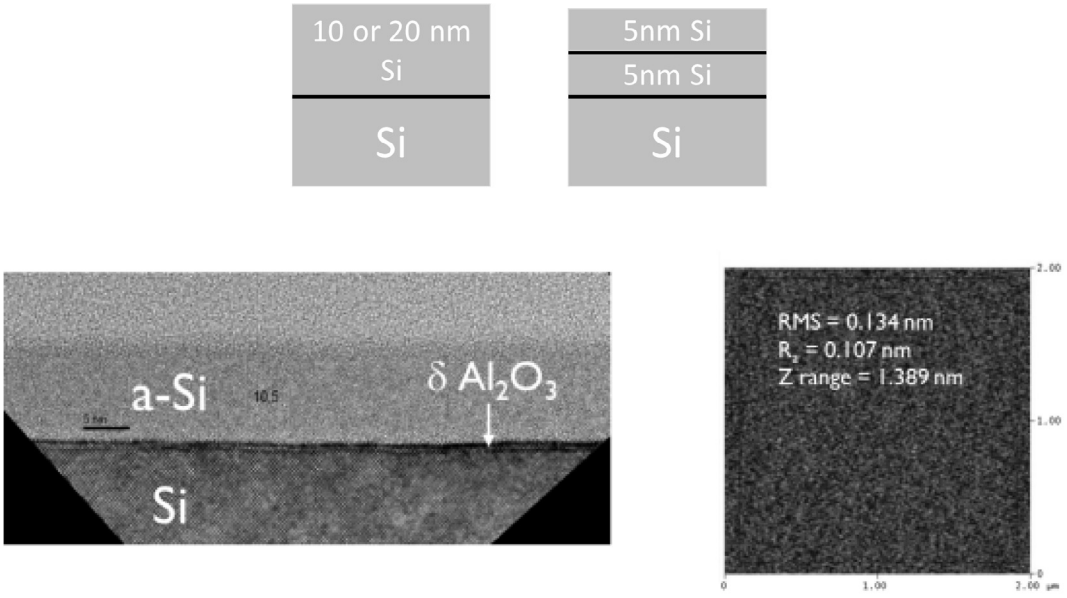

Fig. 1. Schematic representation of the two different structures analyzed together with the TEM cross section and the AFM image from the as deposited single Al-delta layer covered by 10 nm a-Si.