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Time-Resolved Grazing Incidence X-Ray Absorption Spectroscopy for the In Situ Investigation of the Initial Stages of Sputter-Deposited Copper Thin Films

Dirk Lützenkirchen-Hecht,* Jan Stötzel, Justus Just, Oliver Müller, Benjamin Bornmann, and Ronald Frahm

The sputter deposition and the growth of thin copper films on float glass substrates are in situ studied using grazing incidence, reflection mode X-ray absorption fine structure spectroscopy with subsecond time resolution. The experimental data are compared with model calculations, assuming the presence of crystalline, face-centered cubic metallic Cu nanostructures. From a detailed analysis of the measured spectra, the film thickness as well as the surface roughness is determined, leading to a detailed understanding of the films growth as a function of the sputter deposition time. In particular, different stages of film growth can clearly be distinguished from the fits of the experimental data. The results suggest the formation of isolated, approximately nm-sized copper clusters in the initial phase of the film deposition for the first few seconds, a coalescence phase with a nominal thickness of about 1.4 nm for the subsequent ≈5 s, and finally 3D growth of the Cu crystallities in the film for later stages of film growth. Further prospects of the methodology are given.

1. Introduction

Sputter techniques use the bombardment of a target material with accelerated ions, the release of target atoms into the gas phase, and their precipitation on an eventually heated or cooled substrate to prepare thin films of high quality and good adhesion.[9] Due to the versatility of the involved processes, sputtering has become one of the most popular methods to deposit metals, alloys, as well as oxides, nitrides, or carbides by simply adding a reactive component to the sputter gas.[10] In general, the structure and the morphology of the prepared films strongly depend on the details of the deposition conditions such as the combination of film and substrate materials, the sputter gas composition, pressure and flow, and the temperature of the substrate (see, e.g., other studies[8–13]). Accordingly, the physical and chemical properties of the deposited materials can be tailored by a variation of these influential process parameters, so that sputtering processes become a key technology for the preparation of functional materials.

For in situ studies of sputter deposition processes or in particular an in situ process control of the growing films, ion and electron techniques are unsuited because of the high gas pressures needed for sputtering. Photon-in photon-out techniques such as grazing incidence X-ray scattering, X-ray reflectometry, and X-ray absorption spectroscopy can overcome these limitations and may provide detailed insights into the growth mechanisms and the structural properties of sputtered thin films in situ (see, e.g., various studies[8–13]).

Due to the weak interaction of X-rays and matter and the extremely small amounts of matter involved, in situ X-ray studies of nanometer thin films have been almost exclusively done using synchrotron radiation, in particular, for real-time investigations.[8,9,11,13] Recent in situ X-ray scattering studies using the latest generation of microfocus X-ray anodes and modern pixel detectors that allow a time resolution of some few seconds are worth mentioning.[14,15] In this context, X-ray absorption spectroscopy (XAS)[16] is another important analytical method: In contrast to X-ray diffraction, which relies on the long range-order symmetry of crystals, XAS provides information on the atomic short range order such as the bond distances and...
coordination numbers of the atoms situated around the X-ray absorbing atom,\textsuperscript{[16]} and it is therefore inherently suited for investigation of nm-sized structures, such as thin films in the early stages of film growth. Quick-scanning extended X-ray absorption fine structure spectroscopy (EXAFS) brings time resolution to XAS experiments and thus allows to follow dynamic structural changes of matter.\textsuperscript{[17]} Recent experimental developments allow acquisition times in the range of some few milliseconds only,\textsuperscript{[18,19]} so the combination of such a fast-scanning X-ray monochromator with the grazing incidence geometry\textsuperscript{[20]} allows to follow surface reactions on the subsecond timescale.\textsuperscript{[21]} A detailed evaluation of the measured data thus allows to determine the short-range-order structure of the growing films, their surface, and interface roughness, as well as the chemical valence of the X-ray absorbing atoms.\textsuperscript{[22,23]} In the present study, we want to follow the initial stages of growth of thin copper films during sputter deposition in pure Ar atmospheres with time-resolved, surface-sensitive XAS experiments. Due to the ongoing miniaturization of integrated circuits, the well-controlled growth of extremely thin copper films is of utmost importance, for example, for the reliable fabrication of nanosized interconnection layers.\textsuperscript{[24,25]} Furthermore, small Cu clusters on various supports (substrates) are catalytically highly active, for example, for methanol synthesis\textsuperscript{[26]} or the reduction of NO\textsubscript{x} in three-way catalysts for automobiles.\textsuperscript{[27]}

2. Results and Discussion

The course of a typical sputter deposition experiment is shown in Figure 1a. As shown, the reflectivity $R$ of the float glass substrate is small prior to any Cu deposition due to the incidence angle of $\Theta = 0.225^\circ$, which is slightly larger than the critical angle of total reflection for glass in the entire energy range from 8900 to 9400 eV measured here. For comparison, $\Theta$, amounts to values slightly below 0.2° only, with a decreasing trend with increasing energy, for example, about 0.18° at 9450 eV photon energy. After initiation of Cu sputtering for $t = 0$ s, in general, a continuous, fast increase in reflectivity is observed, and furthermore, the Cu K-edge is clearly visible at 8980 eV. For larger deposition times, the amplitude of the EXAFS fine structure oscillations above the Cu edge develops with time as well, with a pattern typically for metallic copper as expected. The details of the changes observed in the spectra can more clearly be followed in Figure 1b, where a single spectrum is plotted in intervals of two seconds, so that the development of the X-ray absorption fine structure typical for copper can easily be seen.

In contrast to transmission mode EXAFS spectroscopy, the quantitative evaluation of the measured reflection mode X-ray absorption data is not straightforward, as both the real ($\delta(E)$) and the imaginary part ($\beta(E)$) of the energy-dependent refractive index $n(E) = 1 - \delta(E) - i\beta(E)$ of the growing film and the substrate contribute to the reflectivity signals depending on the energy and the incidence angle.\textsuperscript{[16,20,22]} Furthermore, for a thin film of a substrate, the roughness at the vacuum side surface as well as at the inner interface are decisive for the distribution of the X-ray absorbing atoms within the penetration depth of the beam, and the situation dynamically changes during film growth.\textsuperscript{[22]} Therefore, if the X-ray penetration depth is larger than the film thickness as in the present situation, it is not possible to extract the absorption coefficient of the film material directly from the measured reflectivity EXAFS spectra. To obtain quantitative structural information on Cu film growth, we therefore modeled the measured data on an ab initio basis.\textsuperscript{[22,23,28]} In particular, we have calculated the energy-dependent reflectivity $R(E)$ using the Fresnel theory and the distorted wave born approximation (DWBA), including surface and interface roughness, utilizing the complex index of refraction calculated from a transmission EXAFS spectrum of a polycrystalline reference foil.\textsuperscript{[22]} As shown recently, a refinement of the input parameters of these calculations yields both the film thickness and its roughness with high accuracy.\textsuperscript{[22,23]} All fit lines are shown in Figure 1b, and some typical fit results for four different stages of the copper film growth are shown in Figure 2. Here, both the reflectivity
spectra \( R(E) \) and the extracted, \( k^2 \)-weighted reflectivity fine structure oscillations \( \chi_R(k)^* k^2 \) are shown. As shown, the calculated (i.e., fitted) data match the experimental data well over the entire thickness range of the deposited film, which suggests that the film structure is well-described by polycrystalline metallic copper from the initial stages of deposition with subnanometer thickness to a film of about 10 nm thickness after 30 s of deposition. It is noteworthy that even after only 2 s of sputtering the EXAFS fine structures typical for copper are well reproduced in the experiment, suggesting the presence of small metallic clusters with less than 1 nm size, corresponding to an equivalent of less than only four monolayers (Figure 2a). Here, the overall shape of the experimental \( R(E) \) is well reproduced by the calculation below and above the Cu K-edge, implying identical values for the thickness \( t_f = 0.79 \) nm, that is, only \( \approx 3 \) monolayers, and the roughness \( \sigma_f = 0.79 \) nm at this growth stage. However, the amplitude of the reflectivity fine structure \( \chi_R(k)^* k^2 \) shows a remarkably larger amplitude in the range between \( \approx 6 \) and \( 8 \) Å\(^{-1}\).

This trend can also be seen by a closer inspection of Figure 2b,c, however, with a decreasing trend with increasing thickness from about 2 nm (\( \approx 8 \) monolayers) and 4.5 nm (18 monolayers), respectively. The observed discrepancies might be related to the extremely small size of Cu deposits in the early stages of deposition, and an accordingly larger fraction of Cu atoms situated on the surfaces of these small clusters, with a lowered coordination number of neighboring atoms and a larger vibrational freedom, that both lead to a reduced amplitude of the EXAFS fine structure oscillations and are less significant with increasing size of the clusters and film thickness, respectively. More detailed calculations and modeling are, however, required to include this in the data evaluation.

In Figure 3, the evaluation of film thickness and vacuum-side surface roughness deduced from the fitting of the reflection mode XAS spectra in the first 14 s of sputter deposition is
compiled as a function of the sputter time. As expected for the sputter deposition process with constant pressure and sputter current, the thickness increases linearly with deposition time, with a growth rate of 0.30 nm s\(^{-1}\), corresponding to about one monolayer of copper per second. It is important to note that the growth rate can be deduced from the analysis of the experimental data as described here, so no a priori knowledge of the atomic flux impinging on the substrate is required. Furthermore it should be noted that all of the XAS spectra recorded with 5 Hz (i.e., 100 ms for each spectrum) were evaluated, so the growth of each monolayer can be sensitively monitored using fast-scanning EXAFS experiments here. Keeping in mind that sputtering is in general assumed to be a high-deposition-rate coating process, it is important to note that almost ten spectra are recorded during the growth of every individual monolayer.

As shown in Figure 3, the film roughness also linearly grows within the first 3 s of film deposition (corresponding to the first five monolayers); however, a constant roughness of about 1.4 nm is found for the subsequent 5 s, where the film thickness continuously increases from about 1.4 nm to about 3.0 nm, that is, in the range from \( \approx 6\)–12 monolayers. In the later course of film growth, again, a slower increase of the roughness is observed for film thickness larger than \( \approx 3.0 \) nm.

The observed behavior of film thickness and roughness can be explained by the different stages of growth, as schematically shown in Figure 3. In the first few seconds of film growth, the presence of small clusters containing only few atoms corresponding to a critical size is very likely, and those clusters grow in the course of the sputter process\([1,11,14,29,30]\), leading to a parallel increase in nominal thickness and roughness. In the subsequent coalescence stages, thickness further increases, but the substrate is entirely covered with nuclei, which results in stagnant roughness, before 3D growth is initiated on a continuous metal film, with a directly linked roughness increase.\([14,29,30]\) It should be mentioned here that Cu metal film slowly grown on heated graphite by thermal evaporation behaves very similar; however, the transition between nucleation and cluster growth and coalescence takes place at a slightly larger thickness of 2 nm (about eight equivalent monolayers), and the percolation threshold occurs at about 9 nm thickness.\([14]\) Compared with the present thresholds of 1.4 and 3 nm for coalescence and percolation, respectively, the faster deposition by sputtering obviously leads to smaller Cu clusters and continuous Cu films at a reduced thickness.

3. Conclusion and Future Prospects

In conclusion, we have demonstrated that detailed in situ studies of thin-film sputtering are feasible using time-resolved grazing incidence XAS. Thanks to the outstanding performance of state-of-the-art quick-scanning monochromators, several data sets can be measured in the course of the deposition of a single monolayer, allowing extremely precise investigations of thin-film growth processes, from the first adsorbed atoms to a continuous film of several ten nanometer thickness. Taking the present study as an example, we have shown that small Cu clusters with a size of up to about 1.4 nm are formed during the initial stages of film deposition within a time period of about 3 s, followed by a coalescence stage characterized by a constant roughness and a thickness in the range of \(\approx 1.5\)–3.0 nm and a slower increase in roughness when the Cu film thickness further increases and 3D growth is observed.

The observations are important, for example, for the reliable preparation of interconnects with minimized size (thickness) in integrated circuits by sputtering techniques, where a continuous structure with best-possible roughness parameters and accordingly optimized electrical resistivity is mandatory for further downscaling of the circuit architecture.\([24,25]\) In contrast, the coating of a metallic catalyst consisting of small, nm-sized, isolated particles is of key importance for the preparation of supported catalysts with high activity for their specific use,\([31]\) and thus, it is essential to identify the optimum preparation conditions as well. The proposed methodology appears extremely useful to allow the identification of optimized processing conditions and the supply of nanostructured materials with tailored structures and related properties. Time-resolved, in situ grazing incidence XAS yields fundamental insights into the formation mechanisms of the thin film/substrate interface and can even be applied under harsh experimental conditions in terms of aggressive, corrosive gases, or temperatures, and its application appears thus promising for future studies, in particular also for reactive sputtering processes and for solid–liquid interfaces.

4. Experimental Section

The experiments described here were conducted at beamline X10DA (SuperXAS beamline, Paul Scherrer Institute, Swiss Light Source)\([32]\) and the Quick-EXAFS endstation P64 at the PETRA III storage ring (DESY, Hamburg, Germany).\([33]\) At both beamlines, oscillating S(111) channel-cut monochromators were used, and N\(_2\) gas-filled ionization chambers were used as detectors for the incident and the reflected intensities. Slit systems were used to define the incident beam (0.1 mm vertical (v) \(\times 1\) mm horizontal (h) size) and clean the reflected beam (0.3 mm (v) \(\times 2\) mm (h)), respectively. X-ray absorption data were collected in the grazing incidence geometry using incidence angles between 0.1° and 0.3° at the Cu K-edge (8979 eV). The in situ X-ray experiments were conducted using a slightly modified miniaturized deposition chamber (diameter \(\approx 100\) mm) with a turbomolecular vacuum pump (base pressure about \(10^{-6}\) mbar), polyimide X-ray windows, and a magnetron sputter source (55 mm diameter) with a high-purity Cu metal target under Ar atmosphere of typically \(10^{-3}\) mbar.\([34]\) Deposition took place on thoroughly cleaned float glass substrates (\(\approx 15\) mm width, 25 mm length, and 4 mm thickness) placed in a distance of about 20 mm to the magnetron. To achieve high sensitivity for XAS experiments, the incidence angles were set slightly above the critical angle of total reflection of the glass substrate, but below that of the growing Cu film, so that total reflection of the X-rays occurs at the film–vacuum interface, and X-ray reflectivity substantially increases in the course of the deposition accordingly. XAS measurements were carried out with oscillation frequencies between 1 Hz (500 ms for each XAS spectrum) and 10 Hz (50 ms), and the data acquisition was started several seconds prior to the start of film deposition. A Cu metal reference foil was measured simultaneously with the growing film between the second and third ionization chamber for energy calibration.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data presented in this study are available from the corresponding author upon reasonable request.

Keywords

grazing incidence EXAFS, roughness evolution, sputter deposition, thin-film growth, time resolution

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