Thin Solid Films 519 (2011) 2664–2667

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Plasmon resonance shift during grazing incidence ion sputtering on Ag(001)

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ARTICLE INFO

Available online 17 December 2010

Keywords:
RAS
Plasmon resonance
Ion beam induced nanopatterning
Roughness analysis

ABSTRACT

Grazing incidence ion sputtering was used to create shallow ripple patterns on a Ag(001) surface. The anisotropic plasmon resonance associated with this ripple pattern can be sensitively measured with Reflection Anisotropy Spectroscopy. A slight red shift of the resonance energy is observed with increasing ion fluence. The observed resonance feature is described well with a skewed Lorentzian line shape. This line shape is the small roughness length scale limit of the Rayleigh Rice perturbation approach. The width of this line shape is directly related to imaginary part of the dielectric function, which shows a roughness induced reduction of the electron mean free path. The observed change in resonance energy and strength with ion fluence is discussed.

1. Introduction

Ion beam sputtering is a well established technique for the creation of a ripple pattern on a wide variety of surfaces. These patterns are the result of a balance between heterogeneous ion sputtering and diffusion processes on the surface [1]. The limited interlayer diffusion on Cu and Ag (001) surfaces strongly influences the pattern formation [2,3]. Ripples are only observed for grazing incidence ion sputtering [3,4]. The fast and in-situ characterization of such structured surfaces is an increasingly important task to understand the underlying mechanisms in pattern formation. Optical methods like light scattering have been used to characterize the statistically averaged properties of (periodically) rough surfaces [5–7]. The specular reflected beam also contains this information on the surface. Scatterometry uses this to characterize periodic structures from the polarization state of the reflected beam [8] Such measurements are analyzed by the computationally demanding Rigorous Coupled Wave Analysis approach. Alternatively, the Rayleigh Rice Theory (RRT) can be used for the analysis if the amplitude of the periodic structures is much smaller than the wavelength of the light. This requirement stems from the fact that RRT is a perturbation approach to the solution of Maxwell's equation at a sharp interface. We showed the applicability of RRT for the characterization of ion beam induced periodic etch features on a Ag(001) surface [9]. The surface plasmon resonance induced by such periodic patterns allow a sensitive, in-situ detection of the pattern characteristics with a technique like Reflection Anisotropy Spectroscopy (RAS).

The relation between a surface plasmon resonance and surface roughness was explored by Kretschmann and Kröger [10]. Their formulation of this optical response was generalized to oblique incidence reflection by Beaglehole [11]. Recently, Franta and Ohlidahl [12] reformulated and further generalized this reflection problem. The latter approach was successfully employed to analyze the recorded anisotropic plasmon resonance during ion sputtering of a Ag(001) surface [9]. The analysis of the recorded optical spectra shows a change in periodicity of the nanopattern with ion fluence. The average length scale of the nanopattern is found to be above 200 nm. This allowed the straightforward determination of the periodicity. In this paper we will present the small roughness length scale limit of the RRT approach for anisotropy measurements. In this regime, the recorded spectra are well represented by a skewed Lorentzian line shape. This enables to characterize the pattern formation with three variables, its amplitude, position and width. The width of this line shape is directly related to the actual dielectric function at the surface and shows a broadening as a result of a finite size effect. Although the energy position reflects the length scale, its relation is complex. The amplitude will be shown to be related to both roughness amplitude and its length scale.

2. Experimental results

The ion beam erosion experiments were performed on a single crystalline Ag(001) sample in a UHV system [9]. A RAS instrument is used to measure the normalized difference in reflectivity r of two orthogonal directions on the surface:

$$\frac{\Delta r}{r} = 2\frac{r_{\perp} - r_{\parallel}}{r_{\perp} + r_{\parallel}} \tag{1}$$

A home built RAS instrument based on a Photo Elastic Modulator (PEM) is used [13,14]. A lock-in is tuned to the second harmonic of the PEM frequency to measure the real part of Eq. (1). The parallel direction is chosen with respect to the incident ion beam.

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0040-6090
doi:10.1016/j.tsf.2010.12.045

Fig. 1 shows the optical reflection anisotropy spectra during bombardment of a Ag(001) surface with 2 keV Ar ions at a polar angle of incidence of 80° with the normal along the <110> azimuth. An ion current of 5 μA/cm^2 measured at normal incidence was used while the substrate was at a temperature of 320 K. Grazing incidence sputtering results in a plasmon resonance that grows with sputter time and displays a small red shift of its resonance energy. The value of the resonance energy indicates that the characteristic periodicity of the nanoripples is considerably smaller than the wavelength of the light used [15].

3. Optical characterization of nanostructured surfaces

The change in reflection as a result of a rough interface can be described by the Rayleigh Rice approach. Using the notation of Franta and Ohlidahl [12], this perturbation can be written for a normal incident light beam as:

$$\hat{r}_{\perp,\parallel} = \hat{r}^{(0)}_{\perp,\parallel} + \sigma^2 \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \hat{f}_{\perp,\parallel}\left(\vec{K},k_0\right) \times w\left(\vec{K}\right) d\vec{K} \tag{2}$$

where $\hat{r}^{(0)}_{\perp,\parallel}$ is the reflectivity of the unperturbed surface, σ the rms value of the surface height and w the normalized Power Spectral Density Function (PSDF), spanned by the spatial wave vector $\vec{K}$ of the surface. The light interaction is determined by the kernel $f_{\perp,\parallel}$, which depends on the wave vector of the incident light k_0 and $\vec{K}$. With the normalized parameters

$$\hat{b} = \sqrt{\left(\frac{k_0}{K}\right)^2 - 1} \tag{3}$$

$$\hat{c} = \sqrt{\left(\frac{k_0}{K}\right)^2 \cdot \epsilon - 1} \tag{4}$$

$$K = \sqrt{K_\perp^2 + K_\parallel^2} \tag{5}$$

the kernel $f_\perp$ for normal incidence reflection can be written as:

$$\hat{f}_\perp(K_\parallel) = -2k_0 r^{(0)}|K| \left(\frac{k_0}{|K|}\sqrt{\epsilon} + \frac{\left(\hat{b}-\hat{c}\right)\left(\left(\frac{K_\parallel}{K}\right)^2 + \hat{b}\hat{c}\right)}{1+\hat{b}\hat{c}} \right) \tag{6}$$

For $\hat{f}_\parallel$ an analogous expression is found.

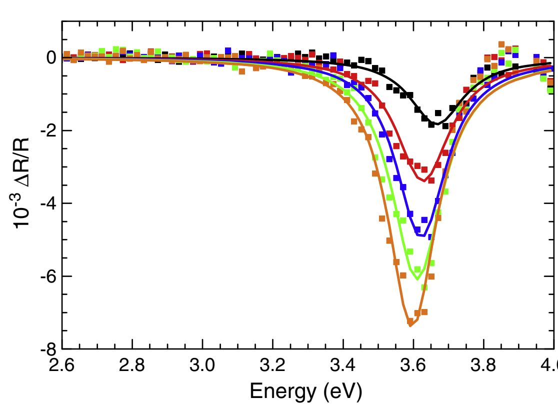

Fig. 1. (symbols) RAS spectra obtained during Ar$^+$ ion sputtering at a polar angle of 80° with the normal. The spectra displayed were obtained during a total sputtering time of 960 min. and are at an interval of 180 min. The solid line represents the fit of a skewed Lorentzian as discussed in the text.

In the displayed RAS measurement an anisotropically rough surface on an optically isotropic substrate is probed. The RAS spectra can be related to the RRT by:

$$\frac{\Delta r}{r} = \frac{\sigma^2}{\hat{r}^{(0)}} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \left(\hat{f}_\perp - \hat{f}_\parallel\right) w\left(\vec{K}\right) d\vec{K} \tag{7}$$

Only the difference in the kernel $\hat{f}$ for the two orthogonal directions is required, eliminating all isotropic contributions:

$$\hat{f}_\perp - \hat{f}_\parallel = -2k_0 \hat{r}^{(0)}|K| \frac{\left(\hat{b}-\hat{c}\right)}{\left(1+\hat{b}\hat{c}\right)} \cdot \cos 2\phi \tag{8}$$

The angle ϕ represents the direction of $\vec{K}$ with respect to the parallel direction. The cos2ϕ term selects the anisotropic part of $w\left(\vec{K}\right)$. Roughness contributions parallel to the ion beam are represented by a negative signal in the RAS spectra, while the perpendicular contribution provides a positive response.

Fig. 2 shows the influence of the average periodicity on RAS spectra for a Gaussian roughness distribution. For an average spatial wave vector of 10 μm^{-1} and below, the RAS spectra show a considerable change in resonance energy, width and intensity. Note the slight feature at 3.3 eV, which is not observed in the experimental data, see Fig. 1. This is due to the use of the Palik data [16] of Ag in this calculation. At this energy, two datasets were merged in this table leading to a slight discontinuity. A spatial wave vector above 10 μm^{-1} changes the intensity of the resonance, while its resonance energy shows a negligible shift. The small sensitivity of the resonance energy

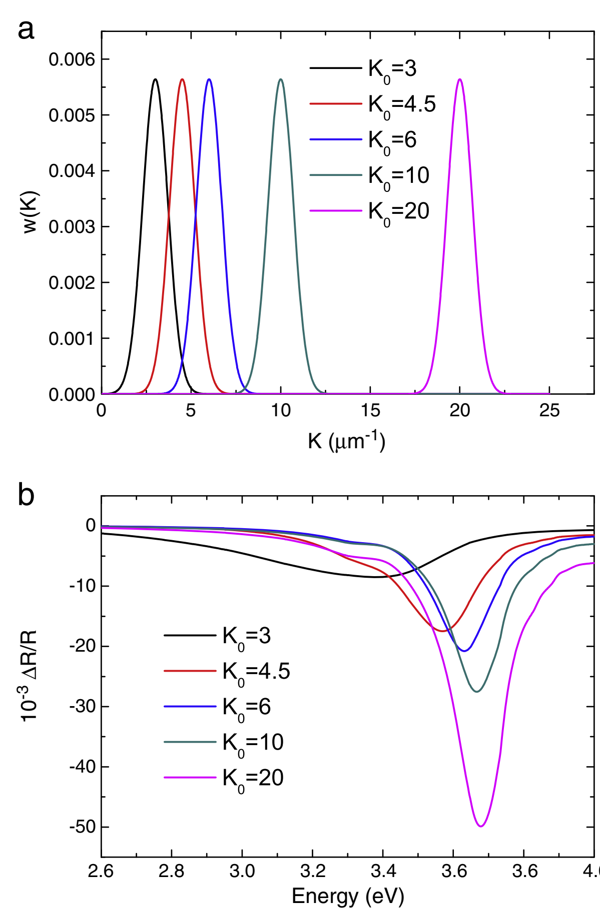

Fig. 2. a) A Gaussian spectral density distributions with different average spatial wave vector $\vec{K}_0$. b) Calculated RAS spectra for the various spectral density distributions displayed in a).

towards the periodicity in this range is well known and is directly obtained in the RRT approach for $K \gg k_0$. This fact allows to simplify the anisotropy of the kernel in this range:

$$\hat{f}_{\perp} - \hat{f}_{\parallel} = -2ik_0\hat{r}^{(0)}\left|\vec{K}\right|\frac{\epsilon - 1}{\epsilon + 1}\cos 2\phi \tag{9}$$

The kernel is reduced to a modulation of the plasmon optical resonance function $\frac{\epsilon-1}{\epsilon+1}$. Both rms roughness and spatial periodicity contribute in a similar way to the strength of this kernel. The anisotropic optical response is found by integrating the product of the kernel and the specific PSDF:

$$\frac{\Delta r}{r} = -2ik_0\sigma^2\frac{\epsilon - 1}{\epsilon + 1}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left|\vec{K}\right|\cos 2\phi\, w\left(\vec{K}\right)d\left(\vec{K}\right) \tag{10}$$

For a 1D ripple pattern with a Gaussian distribution centered around a spatial wave vector K_0 this integration leads to:

$$\frac{\Delta r}{r} = -2ik_0\sigma^2 K_0\frac{\epsilon - 1}{\epsilon + 1} \tag{11}$$

Note that this result does not depend on the actual width of the distribution. Only the product of the rms roughness and the average spatial wave vector K_0 determines the amplitude. This indicates that one cannot distinguish between the two in the small roughness region. This simplification is only obtained for the anisotropic reflection of an anisotropic pattern. On an isotropic randomly rough surface the isotropic contributions to the kernel show additional features [10].

The dielectric function of silver around the resonance energy for several literature datasets [16–18] is displayed in Fig. 3. In the limited energy range of the observed resonance energy, the dielectric function can be approximated by: $\epsilon = -1 + \alpha(E - E_0) + i\gamma$ with E_0 the energy for which $Re(\epsilon) = -1$. The value of $\alpha = 6eV^{-1}$ is very similar for the three datasets, while the value of γ is considerably larger for the Palik dataset. The use of this dielectric function in Eq. (11) gives for the real part of the optical anisotropy:

$$\frac{\Delta R}{R} = -4\sigma^2 K_0 k_0\frac{\gamma/\alpha^2}{\Delta E^2 + (\gamma/\alpha)^2} \tag{12}$$

In this, ΔE is the energy difference with respect to the resonance position, $E - E_0$. For small scale roughness, the measured plasmon resonance is only sensitive for the product of the average reciprocal roughness periodicity, K_0 and the roughness variance σ^2. A smaller roughness length scale enhances the optical response. Note that the use of a Drude form for the dielectric function would give a similar result, albeit that 3 parameters are required to characterize the Drude line shape. This results in a strong coupling between two of the parameters avoided by the approximation used above.

The skewed Lorentzian was fitted to the measured data and was found to represent the dataset very well as displayed in Fig. 1. Also the resonance energy E_0 was used as a fit parameter to accommodate for the observed slight red shift. This red shift from the energy position of 3.68 eV (see Fig. 3) indicates that the approximation $K >> k_0$ is no longer valid. However, the goodness of the fit shows that the skewed Lorentzian line shape can still be used and provides a good method to establish the resonance energy, the strength and the width of the line shape. These provide a valid experimental parameter set and they will be interpreted along the lines of Eq. (12).

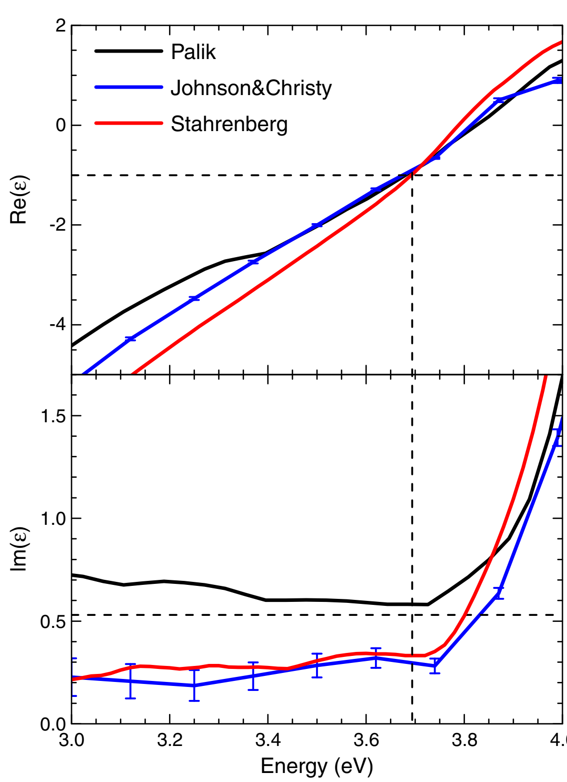

Fig. 3. Dielectric function of Ag as reported by Palik [16], Johnson and Christy [17] and Stahrenberg et al. [18].

4. Time evolution of the induced roughness

The change in the RAS spectra with sputter time is quantified by the fit parameters displayed in Fig. 4. The width of the resonance feature is about constant, providing $\gamma = 0.53$. This value is quite similar to that found in the Palik data, but considerably higher than the more accurate values reported by Johnson and Christy [17] and Stahrenberg [18], see Fig. 3. We attribute this to a reduced electron mean free path on the silver surface as a result of the induced roughness. To verify this, we also measured the RAS signal after sputtering at 250 K. This gives a similar pattern with a smaller characteristic length scale [3]. The RAS spectrum shows a resonance energy at 3.68 eV, i.e. at $Re(\epsilon) = -1$ and a peak width with $\gamma = 0.65$. This width is 20% higher than at 320 K, attributed to a further reduced electron mean free path as a result of the smaller roughness length scale at the low temperature.

The development of the resonance energy with time directly reflects the increase of the average roughness length scale. The fit with a skewed Lorentzian allows to establish the resonance energy with great accuracy. It is tempting to translate the resonance energy shift into a length scale. However, we found in simulations a strong correlation between the average spatial wave vector and the width of the distribution with respect to the resonance energy. As a consequence, without knowledge of the distribution width, the resonance energy cannot be used to extract the periodicity as was possible for less grazing incidence ion sputtering [9]. The goodness of fit should not hide the fact that Eq. (12) is used outside its derivation limits.

The increase of the strength of the resonance is reflected by the parameter $\sigma^2 K_0$. Because the ripple periodicity increases with sputter time, the observed change is the result of an increase in the roughness variance. An estimate of the surface roughness can be obtained by assuming a reasonable ripple periodicity. For a periodicity of 100 nm a roughness of $\sigma = 0.4$ nm is evaluated for the highest ion dose. This value is very reasonable in view of previous results [3]. The observed linear increase of $\sigma^2 K_0$ with sputter time indicates that $\sigma \propto t^{\beta}$ with $\beta > 0.5$. A much higher value of this critical exponent is not likely.

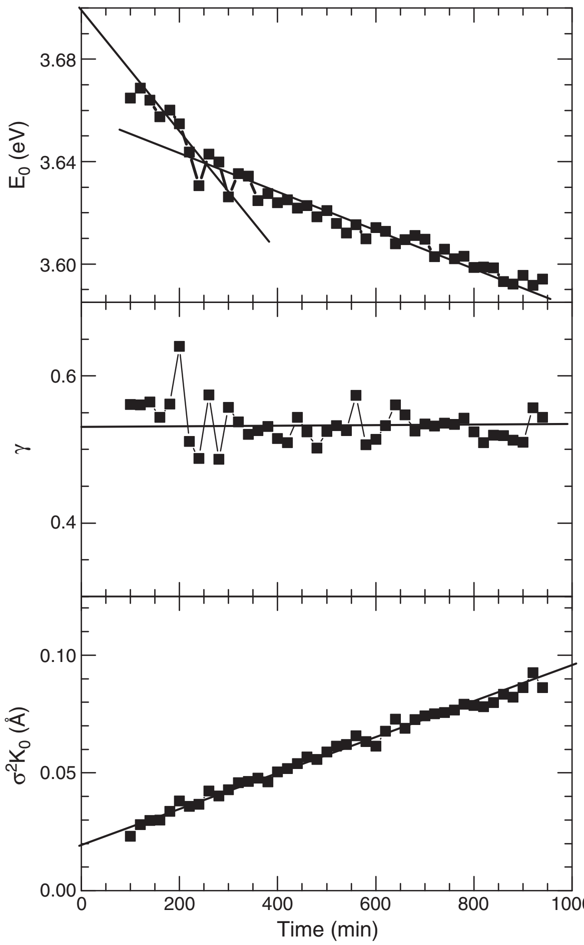

Fig. 4. Result of the fit of the skewed Lorentzian on the measured RAS spectra. Shown are the time development of the resonance energy E_0, the width γ and the amplitude $\sigma^2 K_0$. The lines are a guide to the eye.

5. Conclusion

Grazing incidence ion sputtering of a Ag(001) surface results in a ripple structure whose time development was measured with RAS. A slight red shift of the plasmon resonance energy with time is observed in the optical spectra. The average periodicity of these ripples is around 200 nm, i.e. at the lower border for the observation of a resonance shift as a result of surface roughness. A small length scale limit of the RRT approach was derived that shows that in this limit the influence of roughness and periodicity can no longer be distinguished. An appropriate approximation of the silver dielectric function shows that the measured spectra are well represented with a skewed Lorentzian line shape. This line shape enables a quantitative analysis. The width of the measured plasmon resonance shows that the induced ripples alter the actual dielectric function of silver at the surface. This alteration is the result of the reduced electron mean free path as a result of the surface roughness.

Acknowledgements

This research was supported by NanoNed, a national nanotechnology program coordinated by the Dutch Ministry of Economic Affairs. Christoph Cobet and Norbert Esser are gratefully acknowledged for providing their silver dielectric function data [18].

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