

Evaluation of Coatings Produced by Low-Energy Ion Assisted Deposition of Co on Silicon

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Abstract

Ion assisted deposition (IAD) is a commonly used technique in modern surface modification treatments. Ever since the introduction of IAD (IBAD) methods it has been debated whether the low-energy ion beam, intended for the formation of dense coatings on surface, can also cause ion mixing, how it can influence incorporation of admixtures into thin films and on the growth of films under variable ion-to-atom ratios and deposition rates.

The purpose of this study is to determine the influence of 200 and 500 eV Ar⁺ ion beams on the evolution of Co coatings formed on Si by means of IAD, when the ion-to-atom ratio and deposition rate were varied in the intervals of 0.1 - 0.9 and 3.4 - 10.2 × 10¹⁴ at/(cm²s) respectively. The composition of the thin films produced by the IAD technique has been investigated using Rutherford back scattering of 2.0 MeV He⁺ ions. The thickness of the Co layers deposited on Si exhibited major dependencies on ion-to-atom ratio. This decreases with increase of this ratio. The relative amount of argon captured into coatings was two to three times more when the energy of assisting ions increases from 200 to 500 eV. A minor mixing effect is observed in an interface region at both energies applied for IAD. A quantitative evaluation of ion irradiation effects during low-energy IAD of Cobalt on Silicon is given.

Introduction

There is much interest in the deposition of thin films using ion assistance techniques including directed ion beams [1] or plasma sources [2]. Generally such techniques involve simultaneous bombardment of a thin film during deposition with inert gas ions or chemically active ions to achieve a desired composition. Only in the case of self-ion assisted deposition [3] can the presence of a species, desired or not, different to the deposited species be avoided. Although inert gas occlusion in deposited films is well known [4] little quantitative information on its concentration or the effects on film properties as a function of the processing parameters exists [4-6]. The present study represents a step in this direction in which, in a directed ion beam system, the ratio of ion: atom arrival rate and the ion energy were varied when cobalt was deposited in the presence of Ar⁺ ion irradiation and the rates of Co deposition and the Co:Ar ratio were measured as functions of these parameters.

Experimental Methods and Results

The system employed for the current studies has been described in detail elsewhere [7] and consists, essentially, of a high vacuum chamber pumped by diffusion pumps to which is attached two ion sources. Both of these sources are of the broad-beam Kaufman type and one delivers Ar⁺ ions at 1 keV to sputter a plane Co target which provides the Co atom deposition flux. The second source provides an Ar⁺ ion flux at energies from 200 eV to 500 eV to directly bombard the substrate (Si) upon which the Co is deposited.

The target and substrate are so positioned that the Co arrival flux varies with position across the Si substrate but the assisting Ar^+ ion flux varies only slightly over this area. The Ar^+ ion flux variation, as a function of source parameters (energy and total beam current) was measured carefully with a many position Faraday cup arrangement as was the Ar^+ ion current to the sputtered Co target. System pressures were measured with ion gauges and quadrupole mass spectrometers, target and substrate temperatures with embedded thermocouples and the Co deposition rate could be measured with a moveable quartz crystal oscillator.

The main method of determining both the quantity of Co deposited, and hence deposition rate from knowledge of deposition time, and Ar incorporated in films, however, was by Rutherford Back Scattering Spectroscopy [8] using 2 MeV He^+ ions as the probe, after a deposition cycle had been completed. This technique gives accurate and quantitative information on the depth profiles of concentrations of species throughout a film and, by integration, the average concentrations of all species. Such averaged concentrations are presented in the current work. Since the atomic masses of the substrate (Si), Ar and Co are significantly different there is relatively little overlap in the as-received RBS spectra of these components in the Si-film structure and so the atomic concentrations of the species could be determined rather accurately. Although not the main emphasis of the present work examination of the forms of the RBS spectra obtained from Co films deposited without or with congruent Ar^+ ion bombardment assistance revealed significant evidence of atomic mixing at the Si-film interface in the ion assisted case. This well-known, collisionally driven, process might be expected to improve, for example, film-substrate adhesion.

Using the above methods the rate of Co deposition, R_d , was first measured without simultaneous ion assistance at different positions on the substrate for defined target sputtering conditions. The rate of Co deposition, R_{Co} , was then measured for identical target sputtering conditions but with simultaneous application of Ar^+ ion assistance with energy $E_0 = 200$ eV or 500 eV and with a range of ion assistance flux densities, J_i , achieved by varying both the total ion flux from the source and/or assessing the composition of the film at different regions on the substrate. The rate of incorporation of Ar, R_{Ar} , was determined for each case studied.

The main results of these investigations are presented in Figs 1 and 2. Fig. 1 shows the ratio of

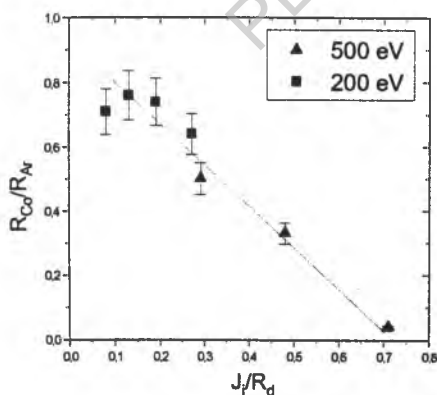


Fig. 1 The ratio of the Cobalt deposition rate with of ion bombardment to that without ion bombardment as a R_{Co}/R_d as a function of the Ar^+ ion flux: non ion Co assisted Co deposition rate ratio J_i/R_d

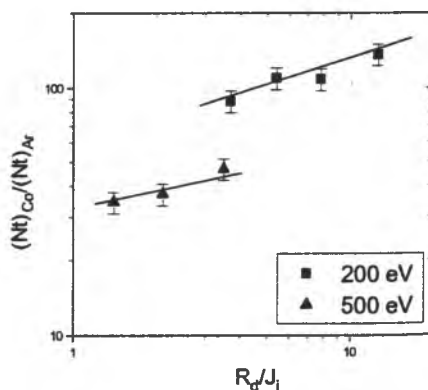


Fig. 2 The depth integrated ratio of the quantity Cobalt deposited to Ar trapped $Nt(Co)/Nt(Ar)$ function of the ratio of the non ion assisted deposition rate to the Ar^+ ion flux R_d/J_i

the Co:Ar deposition rate, R_{Co}/R_{Ar} , as a function of the ion:atom arrival rate ratio J_i/R_d while Fig. 2 displays the ratio of the depth integrated concentrations of Co:Ar as a function of the atom: ion arrival rate ratio R_d/J_i . In Fig. 1 the data for 200 eV and 500 eV Ar^+ ions fall upon the same line but, in Fig. 2, the data for 200 eV and 500 eV Ar^+ ions lie upon different curves. It may be noted that, in both cases, the ion:atom arrival rates were varied by about one order of magnitude.

Theory and Discussion

The effects of ion bombardment are not only to cause atomic displacements and ensuing intermixing of substrate and film components (as noted earlier) and intermixing and spatial homogenisation of film components, but also to introduce, by implantation, bombarding Ar^+ ions into the surface and to simultaneously sputter erode the growing film and incorporated Ar. Following an initial incubation period where ions penetrate and trap in both the substrate and the earliest thickness of the film an equilibrium will be established in which the rate of Ar incorporation by implantation is balanced by sputtering of Ar from the near surface region of the growing film. Under these conditions, as the film continues to grow the Ar concentration, $Nt(Ar)$, and the Co concentration $Nt(Co)$ will become depth independent relative to the film surface.

If the sputtering yield, in equilibrium, of the film is Y and the Ar^+ ion incorporation probability is η , then the following steady-state equations apply:

$$R_{Co} = R_d - J_i Y N^{-1} \quad (1)$$

$$\frac{Nt(Co)}{Nt(Ar)} = \frac{R_{Co}}{R_{Ar}} = \frac{R_d - J_i Y N^{-1}}{J_i \eta N^{-1}} \quad (2)$$

where N is the effective atomic density of the Co:Ar composite film. Eq.1 shows that the net Co deposition rate is the balance between atomic Co deposition and removal, by sputtering of Co, while Eq. 2 simply reflects the requirement that the concentration ratio should equal the 'effective' species deposition ratio. Eq. 1 may be rewritten as:

$$\frac{R_{Co}}{R_d} = 1 - \left(\frac{J_i}{R_d} \right) Y N^{-1} \quad (3)$$

and Eq. 2 may be rewritten as:

$$\frac{Nt(Co)}{Nt(Ar)} = \left(\frac{R_d}{J_i} \right) \frac{N}{\eta} - \frac{Y}{\eta} \quad (4)$$

Clearly Eq. 1 predicts that R_{Co}/R_d should be a linear function of J_i/R_d with a gradient of $- Y N^{-1}$ and Eq. 2 predicts that $Nt(Co)/Nt(Ar)$ should be a linear function of R_d/J_i with gradient N/η and intercept $-Y/\eta$. Apart from a small deviation for small J_i/R_d it is evident that Fig. 1 displays the type of behaviour predicted by Eq. 1. The deviation for small J_i/R_d may be attributed to larger errors in ion flux determination and/or to fast Ar neutral atoms which are backscattered from the sputtered Co target and strike the film but are unrecorded as ions. This would effectively increase J_i and move the data points closer to the linear fit. The fit of both 200 eV and 500 eV Ar^+ ion bombardment to a common line is somewhat unexpected since the sputtering yield for 500 eV might be expected to be substantially larger than for 200 eV ions [9]. It is, however, possible that more data points would modify this result and it

should be noted that as ion flux increases the films become thinner so that deposition rates are less reliably evaluated.

In a similar manner Fig. 2 also corresponds well with the linear function prediction of Eq. 4. For both 200 eV and 500 eV ion assistance a linear fit is rather well obeyed and the gradient for the 200 eV data appears to be slightly larger than that for 500 eV data. This, from Eq. 4, implies that $\eta(200 \text{ eV}) < \eta(500 \text{ eV})$ which is entirely expected since the penetration and incorporation probability would be expected to increase with increasing ion energy [10]. It should be pointed out that Eq. 1, (and hence Eq. 2→4), is only valid for positive R_{Co} where the cobalt deposition rate exceeds the sputtering rate. When these are equal R_{Co} and R_{Ar} become zero and the ratio $Nt(Co)/Nt(Ar)$ is indeterminate. Consequently the apparent intercepts of the $Nt(Co)/Nt(Ar)$ data as $R_d/J_i \rightarrow 0$ have no physical significance. Indeed the results of Fig. 1 suggest that no net film deposition occurred when $J_i/R_d \geq 0.7$, i.e. $R_d/J_i \leq 1.4$ and so, in Fig. 2 concentration ratios in this region of R_d/J_i should be regarded with some circumspection. Moreover when the films are very thin ion penetration into the substrate and species intermixing between film and substrate become increasingly important so that effective values of η , Y and N may vary. Consequently it is the data at larger values of R_d/J_i which is more reliable and, as indicated fits to Eq. 4.

Conclusions

Quantitative measurements have been made of both the net Cobalt deposition rate and the Cobalt: Argon concentration ratio when Co films were deposited with and without simultaneous Ar^+ ion irradiation for Ar^+ ion: Co atom arrival rate ratios ranging from 0.07 to 0.5 and for Ar^+ ion energies of 200 eV and 500 eV. As predicted by simple theory the Co deposition rate decreases with increasing Ar^+ ion flux as a result of sputtering of the growing film and the fractional Ar concentration decreases as the Ar^+ ion flux decreases (i.e. $Nt(Co)/Nt(Ar)$ increases as R_d/J_i increases). This latter behaviour results from the fact that decreasing the Ar^+ ion flux both increases the net Co deposition rate and decreases the Ar^+ implantation rate. The clear conclusion is that, in ion assisted deposition, the assisting ion concentration in the growing film will be reduced by employing large atom: ion arrival rates.

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