NOBLE GAS INCORPORATION IN SPUTTERED AND ION BEAM ASSISTED GROWN
SILICON FILMS

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ABSTRACT

Gas desorption measurements have been performed on sputter deposited silicon films. The sputter gas was argon or krypton. Parameters influencing the incorporation process e.g. bias voltage, substrate temperature and arrival rate ratio of silicon and noble gas atoms have been systematically varied. The films, a-Si and c-Si, have been characterised by various techniques for composition and defect analysis. A model has been applied to describe the composition of the growing silicon layer. Underlying mechanisms like gas-gas sputtering have been studied in separate ion implantation experiments. For a-Si concentrations as high as 6% Ar and Kr have been found. An important effect is the injection of self-interstitial atoms caused by the low energy heavy ion bombardment. It causes the layer to grow without large open volume defects.

INTRODUCTION

Low energy ion bombardment is employed to assist and control silicon film growth [1]. In sputter deposition a negative bias at the substrate causes a considerable flux of low energy (Ar)-ions hitting the growing film. In ion assisted MBE an extra ion gun can provide the required ions. Beneficial effects on the growth process have been reported e.g. Ohmi et al [2] found growth of homoepitaxial Si-films at lower temperature compared to conventional thermal molecular epitaxy (MBE).

Chapman has reviewed the early work on thin film production by noble gas sputtering [3]. Gas release from sputtered silicon films has been reported by Taoufik et al [5] and van Veen et al [6]. Results on the basic incorporation processes of noble gas atoms in metals have been reported by Kornelsen [6], Edwards [7] and van Veen [8].

In this article experimental results are presented for gas incorporation in sputtered silicon films. It is tried to model the incorporation process quantitatively.

EXPERIMENTAL

Thin films were produced by sputtering of silicon in a low pressure (0.01-0.1 Pa) argon or krypton plasma similarly as described in [8]. The standard energy of the noble gas ions striking the target was 1 keV and the standard flux amounted to $6 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$. The bias voltage of the substrate could be varied from 0-300 V, and the temperature could be controlled from 350 - 900 K. The ion flux at the substrate varied from $0 - 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$ depending on the bias voltage. The ion flux could be reduced without changing the plasma parameters by applying a pulsed bias voltage to the substrate (duty cycle from 10-100%). The flux of sputtered silicon atoms arriving at the substrate was calibrated by means of a quartz crystal microbalance and by weighing of the deposited film. Films were deposited on

an area of 10 mm diameter. In a modified setup for desorption studies a Si(111) single crystal of 6 mm diameter was used as substrate which could be heated to 1400 K. A desorption apparatus equipped with a low energy ion beam facility [8] was used to perform desorption studies on the elementary processes taking place during incorporation.

Some of the films were produced elsewhere in MBE-apparatus. Standard techniques EDS, RBS, NRA were used for ex-situ composition analysis. Structure analysis was performed by XRD. Positron beam analysis was used to characterise the defects in the films, in particular the open volume defects [9]. Mössbauer spectroscopy has been applied to probe the local environment of the incorporated krypton [10].

INCORPORATION MODEL

The incorporation of the noble gas atoms is initially caused by a process of implantation and trapping. Those atoms that survive subsequent processes as resputtering of the film or gas-gas sputtering contribute to the final gas concentration. The steady-state concentration $c(x)$ in the growing film is given by

$$0 = \frac{d c}{d t} = J_A I(x) + D \frac{d^2 c}{d x^2} + V_s \frac{d c}{d x} - J_A \sigma_g(x) c(x)$$

with J_A = flux of swift noble gas projectiles from the plasma attracted to the substrate; V_s = net growth velocity = $(J_A Y_s - J_s)/N_0$, where Y_s is the sputtering yield of the noble gas particles and J_s the flux of sputtered atoms arriving at the film surface; N_0 is the atomic density; $I(x)$ = the probability of the noble gas being trapped at depth x ; $\eta = \int I(x) dx$ the integrated trapping probability; $\sigma_g(x)$ = the cross section for gas release from the film by irradiation with noble gas ions; D = the diffusivity (thermal or radiation enhanced). The above model takes into account the release of the noble gas atoms by the process of gas sputtering which is a defect-mediated release process. Tsai et al [1] describe defect and noble gas concentrations in deposited films exclusively by diffusion. The model of eq. 1 does not account for effects caused by high incorporated gas concentrations.

RESULTS OF INCORPORATION EXPERIMENTS

Typical desorption spectra obtained for sputter deposited films with argon are shown in figure 1. Substrate temperatures were varied from RT to 600 K. The release is centered at the temperature where crystallization of the film takes place. The release mechanism is simply explained by pushing the noble

Figure 1. Argon desorption spectra obtained for a 45 nm thick sputtered Si-layers on a silicon (100) wafer at a bias voltage of 30 V. The substrate temperature has been varied as indicated. The narrow peak at 970 K corresponds with crystallization.

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Figure 2. Argon concentration in sputter deposited silicon films vs substrate bias voltage.

In sputter deposited crystalline metal films accumulated noble gas concentrations seldom exceed values of 0.2%. These results might indicate that release mechanisms are much more effective for crystalline than for amorphous structures. For thick films it seems that at elevated temperatures the film grows at first crystalline but after having reached a thickness of about 500 nm (with a low gas concentration) the further growth proceeds as amorphous silicon with a high gas concentration. These observations were made with XRD, SEM (on cross sections), RBS and MEIS techniques. For 5 μ m thick krypton sputtered films RBS and EDS analyses showed concentrations up to 6% for 580 K deposited amorphous films and about 0.3% for films deposited at 850 K.

Bias voltage variation results shown in figure 2 indicate very high noble gas concentrations in the energy interval from 20-200 V. Apparently the penetration probability increases considerably at about 20 eV. At bias voltages > 50 eV resputtering occurs causing a reduction of the net growth velocity and therefore a longer exposure of implanted gas atoms to depth dependent release processes.

The noble gas atom/silicon flux ratio varied by using the pulsed bias mode yielded for krypton sputtered amorphous films, at 50 V bias, the concentrations shown in figure 3. The maximum concentration is reached for a Kr/Si flux ratio of 4. Beyond this value release and sputter mechanisms counteract the noble gas accumulation.

Results of low energy penetration and trapping experiments performed on single crystalline silicon are shown in figure 4. It is observed that already at 20 eV ion energy 5% of the ions and at 100 eV the majority of noble gas ions is trapped. The argon desorption takes place in peaks which occur in the temperature interval from 400 to 830 K. The peak at 830 K has been assigned by us to desorption of argon

gas in front of the crystallization front when epitaxial regrowth takes place [8]. For krypton similar results have been obtained. For thick amorphous layers which have accumulated high concentrations of noble gas epitaxial regrowth is hindered by the presence of the gas so that polycrystalline material with bubbles is formed instead.

Substrate temperature variation has no influence on the gas-concentration for $T < 500$ K. Beyond 550 K the concentration of incorporated gas is reduced to values a factor of 20-100 lower because for high T the films grow as crystalline silicon from which release is easier than from amorphous silicon.

Figure 3. Krypton concentration and relative S-parameter measured for 5 μ m thick sputter deposited films vs the Kr/Si flux ratio at 50 V bias and 580 K substrate temperature. The solid line is the result of a model calculation with parameters given in the text.

Figure 4. Desorption results obtained for Si(111) irradiated with very low energy noble gas ions. a) 15-100 eV Ar⁺-ions at a dose of 10¹³ cm⁻². b) Ar- and Kr-trapped fraction vs ion energy.

from monovacancies. Thus at the elevated temperatures mentioned above a considerable fraction of the trapped gas will be thermally released. The remaining gas, i.e. substitutional noble gas atoms, is subject to athermal release processes.

Gas sputtering experiments have been performed on 100 eV Kr pre-implanted into crystalline silicon. Post-irradiation took place with low energy argon ions of energies of 50, 100 and 500 eV. In this experiment two different noble gas ions have been used to distinguish the pre-implanted from the post-implanted noble gas atoms. Figure 5 shows the results. It is clearly observed that 1. the amount of krypton is reduced, and 2. part of the krypton has been redistributed. The peak at 920 K (substitutional Kr-atoms) and at 750 K is reduced, but some growth occurs of a peak at low temperature indicating clustering of krypton. Similar effects have been observed by us for noble gases in metals [11]. Mobile self-interstitial atoms (SIA) injected by the argon ions were found responsible for kick out reactions as follows: KrV (substitutional) + I (SIA) → Kr (mobile interstitial). The cross sections for gas sputtering derived from the dose variation are of the same order of magnitude as found earlier for metals. Therefore it is likely that also in silicon above mechanism is operating.

For the depth dependence of the gas sputtering we used the expression $\sigma_g = \sigma_0 \exp(-x/\lambda_g)$ with λ_g as the attenuation length for gas sputtering corresponding with the escape depth of interstitial noble gas. From the trapping saturation of low energy implanted noble gas measured for high doses it was derived that the escape depth amounted to a constant value of 0.5 nm, and that the cross sections were 0.4, 1.0 and 2.5 10^{-14} cm² respectively for 50, 100 and 500 eV ions. For the sputter deposition experiments we obtained a satisfactory description when the model parameters in eq. 1 were chosen in line with the above parameters for c-Si; $\eta = 0.035$; $\lambda_g = 0.59$ nm; $\sigma_0 = 1.34 \times 10^{-15}$ cm². The trapping factor η is a factor of 10 lower than that in c-Si because considerable thermal desorption of 50 eV implanted Ar in a-Si takes place at 580 K. Also the gas sputtering cross section is a factor of 3 lower than derived for single c-Si. This may be explained by the reduced depth of penetration of "interstitial atoms" in a-Si compared to c-Si.

Figure 5. a) Kr-desorption spectra for Si(111) irradiated with 100 eV $\text{Kr}^+ 1 \times 10^{13} \text{ cm}^{-2}$ and post-irradiated with 100 eV Ar^+ at the indicated doses. b) Trapped fraction of Kr vs the argon post-irradiation dose for 50, 100 and 500 eV.

Positron beam analysis [12,13] was performed on the krypton sputtered silicon layers. The values of the relative S_r -parameter (for crystalline Si $S_r=1$) are shown in figure 3. Basically observation of a high S-value indicates the presence of open volume defects. Very large voids (100 nm size) yield $S_r = 1.10$; small vacancy type defects $S_r = 1.02$. The latter value has also been observed for 750 K annealed amorphous silicon obtained by Si ion bombardment [14]. The S_r -values found

for the sputtered films are similar. It is worth noting that S_r is reduced with the increase of the krypton-content of the film. Values of S_r for molecular beam deposited amorphous silicon (at 250 °C) are very high, $S_r = 1.14$, which indicates large microcavities. Thus the positron results indicate clearly that ion assisted growth leads to a strong reduction of open volume defects.

Results obtained for silicon films grown by assistance of a 70 eV Ar^+ -ion beam [15] indicate that no open volume defects have been formed during the IBA process. The e^+ diffusion length is shorter than that observed for defect free and field free Si, indicating some e^+ trapping or the presence of an electric field. In case of e^+ trapping it would have to be a trap at which annihilation took place with characteristics quite similar to that of bulk Si, which is not the case for any "pure" open-volume defects. It seems therefore reasonable to assume that the majority of defects in this case would be Ar related such as ArV .

For the first time Mössbauer spectroscopy was applied to Kr-inclusions in Si using the 9.4 keV transition in ^{81}Kr . As an absorber we used 9 μm thick Si-layers containing 6 at % of ^{81}Kr deposited on 15 μm thick Al-foils. The source was dehydrated ^{81}RbI [10]. Preliminary results show that when fitted with a single line and a quadrupole split component and taking into account the quadrupole split nature of the source the spectra show an isomer shift which cannot be explained by a pressure induced reduction of the electron density. Variation of the absorber temperature from 4.2 to 200 K does not show a significant change in the recoilless fraction of both

components indicating that the characteristic Debye temperature must be much larger than 200 K. Measurements as a function of the annealing temperature are currently in progress.

CONCLUSION

Experiments on the incorporation of noble gas in (sputter) deposited films assisted by ion bombardment and low energy implantation experiments demonstrate the important effects caused by the simultaneous injection of Si-atoms (self-interstitials). Open volume defects are reduced or removed by these interstitials and substitutional atoms are converted into higher mobile interstitial gas atoms which will be redistributed or released. A quantitative model is given which describes the incorporation. Low energy noble gas ions are rather easily trapped in silicon. High concentrations found in a-Si are explained by a less effective kick out mechanism for noble gas atoms and less thermal mobility than in c-Si.

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