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Invited Lecture

Laser annealing of sputtered silicon for wafer-bonding applications

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Sputtered silicon is investigated as a bonding layer for transfer of pre-processed silicon layers to various insulating substrates. Although the material appears suitable for low temperature processing, previous work has shown that gas trapped in the pores of the sputtered material is released at temperatures above 350 ^{0}C and further increases of temperature lead to destruction of any bonded interface. Pre-annealing at 1000 ^{0}C before bonding drives out gas and/or seals the surface, but for device applications where processing temperatures must be kept below about 300 ^{0}C, this technique cannot be used. In the current work, we have investigated the effect of excimer laser-annealing to heat the sputtered silicon surface to high temperature whilst minimising heating of the underlying substrate. Temperature profile simulations are presented and the results of RBS, TEM and AFM used to characterise the annealed layers. The results verify that gases are present in the sub-surface layers and suggest that while sealing of the surface is important for suppression of the out-diffusion of gases, immediate surface gas removal may also play a role. The laser-annealing technique appears to be an effective method of treating sputtered silicon, yielding a low roughness surface suitable for wafer bonding, thermal splitting and layer transfer.

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1. Introduction

Current developments in the stacking of CMOS circuitry to make multi-dimensional devices and applications involving temperature sensitive nanocircuitry require a low temperature bonding technology. Historically, much research has been performed in this area for requirements demanded in the fields of MEMS, sensors and actuators, and many applications involving the transfer of silicon layers (which may involve circuitry) to temperature sensitive substrates or to thermally incompatible substrates. A low temperature bonding technology allows a variety of optoelectronic and high-frequency devices on III-V materials to be integrated with silicon-based circuitry [1]. Planarization of metallized circuits which are then coated with a low temperature bonding layer allows transfer without damage to circuitry [2-5]. Other examples include transfer to silicon oxide [6], quartz [7], glass [8], the production of flexible silicon layers on plastic or metal [9], and applications in solar cell technology [10]. Any low temperature wafer bonding process requires a high quality void-free uniform bond over the whole of the wafer surface, with sufficient strength to withstand subsequent handling and processing steps. These may for example involve grinding, polishing and mechanical thinning, mechanical splitting or alternatively annealing treatments for thermal splitting of ion-implanted wafers. Reported bonding techniques include the use of SOG [5], epoxy resins [11], various chemical treatments [12], and the use of surface plasma treatments for bond strengthening [13,14] Whilst some of these processes, for example BCB resins, are undoubtedly effective [15,16], with continuing current trends in the reduction of critical dimensions, bonding methods reliant on dimensional uncertainties of organic adhesives and the need to make precise connections between bonded layers make the use of a clean thin film technique desirable. Furthermore, in applications where good thermal conductivity across the bonded surface is required, polymer resins cannot be used.

Previous work by the present authors suggests that sputtered silicon would be effective for some applications as a low temperature bonding layer [17]. Measurements showed that very smooth layers with a roughness comparable to a polished silicon surface can be sputtered with process temperatures ranging from 70 to 230^{0}C for RF powers between 100 and 800 W respectively. These temperatures were attained within a few minutes from the commencement of sputtering and thereafter remained constant through the deposition time. The sputtered layers could be contact bonded quite easily to silicon or oxide-coated wafers and with plasma treatment and subsequent annealing to a maximum temperature of 350^0C, a high bond strength could be obtained. Problems arose with this material when this temperature was exceeded, since gases trapped during sputtering were released into the bonded interface area, producing voids. When the temperature reached some critical value, generally between 600^0C and 900^0C, a major increase in gas desorption occurred, destroying the bond across the whole wafer surface. The effect is of obvious concern for higher temperature applications but could also be a problem for low temperature applications, since the possible effect on shelf or in-service lifetime is not currently known. The previous studies showed that a sputtered silicon layer could be satisfactorily bonded to an oxide-coated wafer and annealed to 1050 ^{o}C without destruction of the bond interface, provided that the sputter-coated substrate was pre-annealed for 1 to 2 hrs at 1000^0C. Further, it was found that the same result could be achieved by laser-annealing at an appropriate level of power density. This technique allowed hydrogen implantation to be used to subsequently thermally split a thin layer from the sputter-coated wafer [18].

In the present studies, we examine the laser-annealing effect further. Short pulse UV light is particularly suited to raising the temperature of a thin surface film in a controlled manner, without significant substrate heating [19,20]. With silicon films, it is generally used to produce melting and re-crystallisation but has also been used with lower power densities for cleaning (Larciprete et al. [21]) and desorption of carbon and oxygen (Schlemm et al. [22]). Two hypotheses were originally proposed to explain the beneficial effect of laser-annealing sputtered silicon wafers prior to bonding. (a) Trapped gases are embedded in the film during sputtering and these are desorbed from a significant surface layer during annealing. (b) Annealing densifies the film and/or effectively seals the surface, preventing trapped gases from being released into the bonded interface during bond-anneal. The work described here attempts to shed further light on these ideas.

2. Experimental

100 mm diameter silicon <111> wafers were cleaned before and following deposition by immersion in 1:1, H_2O_2: H_2SO_4 at a temperature in the range 75-120^0C for 20 minutes, followed by triple-cycle flushing in particle free DI water followed by spin-drying. For bonding experiments, wafers were also ultrasonically cleaned in modified RCA1 solution: (0.01-0.02:1:5 NH_4OH:H_2O_2:H_2O, 55^0C, 20 min), then rinsed and dried immediately before room temperature bonding.

Wafer substrates were loaded under a Class 10 hood into a Nordiko RF magnetron sputtering system pumped with a diffusion pump and liquid nitrogen trap. The system was fitted with a silicon 200 × 100 mm, 6 mm thick target spaced at 70 mm from a rotating substrate assembly mounted directly above the target. Before sputtering commenced, the vacuum system was evacuated to a base-pressure of around 3.10^{-8} Pa. For sputtering, an RF power of 370 W and argon sputtering pressure 0.47 mbar were used to produce a film of thickness 0.3 micron. Previous experiments [17] had shown these conditions to produce hard dense layers with smooth surfaces suitable for bonding. To minimise the stirring up of particles that could settle on the substrates, the system was vented to filtered dry nitrogen with the flow-rate limited by a needle-valve.

Wafers for thermal-splitting tests were implanted before sputtering with hydrogen, using a H_2 ion fluence of 3×10^{16} cm^{-2} equivalent to an atomic hydrogen ion fluence of 6×10^{16} cm^{-2}, [22]. The energy of implantation was 46 keV, resulting in a calculated projected range of 0.32 micron.

Wafers coated with sputtered silicon were annealed with a KrF Lambda Physik excimer laser (LPX 210i) operating at 248 nm with 25 ns full-width half-maximum pulse duration. The process was performed in a vacuum chamber with a base pressure of 1.5×10^{-4} mbar, the chamber being mounted on a translation stage, which enabled scanning for large area irradiation. The homogenized, semi-Gaussian, 4×12 mm^2 beam profile was scanned along the Gaussian direction, resulting in a ‘multiple pulse irradiation’ scheme. The scanning speed used was 7 mms^{-1} with a pulse repetition rate of 70 Hz. The overlap between any two scan lines was maintained at 7.5% of the pulse width. (In terms of gas desorption, such an experimental set-up has been shown to allow controlled evolution of hydrogen [23]). The pulse density under this scheme was 200 at a given spot. Due to the pulse-to-pulse variation of the excimer laser energy, it is estimated that the measured energy densities have an error of up to 10% [24]. The laser energy density was varied for each separate test, over the range 30 to 150 mJ/cm^2. The irradiated samples were examined by transmission electron microscopy (TEM) after sectioning with a focused ion beam (FIB) and the surfaces with atomic force microscopy (AFM). Rutherford back-scattering spectrometry (RBS), elastic recoil detection (ERD) and elastic back-scattering (EBS) were used to detect the presence of gases trapped below the surface of the sample. Mass spectrometry was used to detect desorption of oxygen, argon, hydrogen, methane and carbon dioxide gases when samples were heated to 750^0C. For these latter tests, a sample about 30mm^2 cut from a treated wafer was clamped securely on a molybdenum holder fitted with ceramic heaters and mounted in a stainless steel vacuum chamber oriented to a second chamber containing an RGA head. The sample temperature was controlled to $\pm2^0$C. Both chambers were pumped with turbo-molecular pumps for a minimum of 3 hrs to less than 10^{-6} mbar, at which point the RGA was switched on and the partial pressures allowed to stabilise. The sample was then degassed for 1 hr at 300 ^{0}C before finally raising the temperature to 750 ^{0}C in 50 ^{0}C steps over a period of 3 hrs. From a knowledge of the system dimensions and pumping speeds, this system would be limited to the detection of about 10^{14} molecules observed over the sampling period of 26 seconds.

A series of non-implanted laser-annealed silicon sputter-coated wafers were test bonded to oxide-coated wafers. These tests showed that satisfactory and repeatable bonding could be achieved for laser energy density levels up 30 mJcm^{-2}, higher values producing surfaces that were too rough to allow bonding. A further series of hydrogen implanted silicon sputter-coated wafers was then laser-annealed at 30 mJcm^{-2} power density, cleaned and bonded at room temperature to oxide-coated wafer substrates and stored for 12 hrs. Following subsequent annealing for 2 hrs at 500^{0}C, these wafers were found to have split cleanly at a depth corresponding approximately to the hydrogen implant depth, to produce a silicon-on-insulator structure.

3. Results

Fig. 1 (a) to (d) shows TEM images of sputtered silicon surfaces, demonstrating the morphological changes that occur at the surface with increasing laser power density. The underlying film structure has a convoluted appearance, suggesting pores of several nanometres dimension. In (a), the surface is quite smooth and surface modifications appear minimal. As the power is increased, melting is apparent, at first in elliptical-like surface structures up to 50 nm major diameter, (b) and (c), and then a more gross deformation with damage extending below the surface, (d). This latter effect was initially observed at an energy density of around 50 mJ/cm.

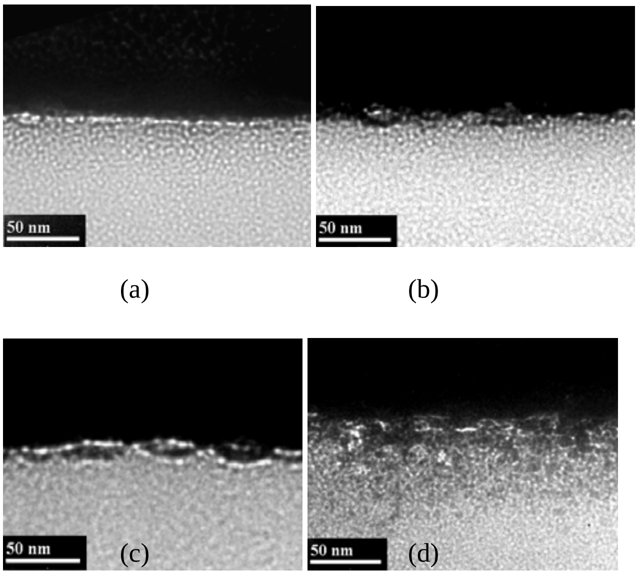

Fig. 1. TEM images of sputtered silicon surfaces for increasing laser energy densities: (a) 10 mJcm^{-2}; (b) 20 mJcm^{-2}; (c) 30 mJcm^{-2}; (d) 50 mJcm^{-2}

Table 1.Variation of surface roughness with laser energy density for sputtered silicon.

Sample number	Laser Energy Density (mJcm^{-2})	R_{rms} nm Mean of 3	R_{max} nm Mean of 3
1	0	0.19	0.50
2	10	0.10	0.27
3	20	0.13	0.44
4	30	0.18	0.74
5	50	0.31	1.41
6	80	1.34	7.79

The change in surface topography with increasing laser energy density was examined also with AFM, confirming these results, (Table 1) where RMS roughness and peak values are shown. The differences are not statistically significant until an energy density of 30 mJ/cm^2 is achieved, when the roughness begins to increase.

Table 2 shows the results of ERD, RBS and EBS for the gases H, Ar, C and O respectively as a function of laser energy density. Because the depth resolution of the techniques is limited, the figures for the gas content are average values throughout the 0.3 micron thickness of the film. For the case of the 80mJcm^{-2} sample, it was possible to fit data to a series of stepwise averages which showed a depletion of argon at the immediate surface (Figure 2). Otherwise, Table 2 shows no significant variation between samples of varying laser energy density. It should also be noted that EBS showed evidence of non-uniform oxidation at the surface for the sample shown in Figure 2. Channelling data for this sample indicated a degree of either epitaxial crystallisation or substrate damage.

Table 2. Atomic percentage of gases averaged over 0.3 micron depth below the sputtered silicon surface

Laser Energy Density (mJcm^{-2})	H (ERD) (at.%)	Ar (RBS) (at.%)	C (EBS) (at.%)	O (EBS) (at.%)
0	5.7	7.5	1.8	0.2
10	4.5	7.6	0.9	0.1
20	5.7	6.9	1.2	0.2
30	5.2	7.7	2.3	0.2
50	5.6	7.8	1.3	0.2
80	3.8	6.0	2.3	0.2

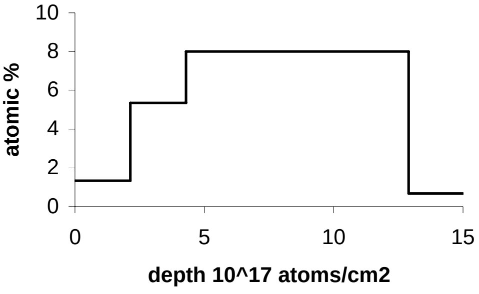

Fig. 2. Fitted depth profile data from RBS for an argon concentration, for80mJcm^{-2} annealed sample 6.

Of the samples investigated, mass-spectrometry with heating of the sample to 750^0C showed no desorption of gas except in the case of the sample which had had no laser anneal treatment (Fig. 2). The gas desorption occurs as a single spike of argon at a temperature of 650^0C

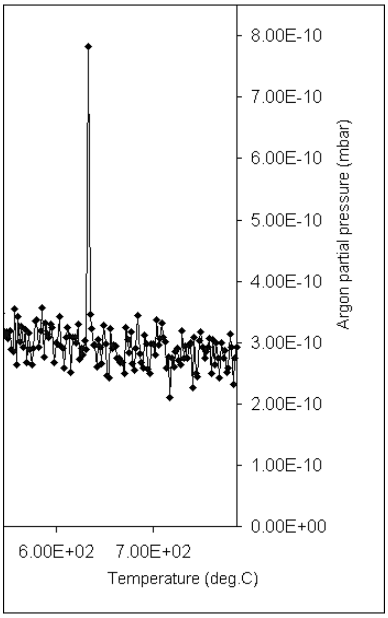

Fig. 2. Argon desorption from sample 36 at 650^0C

4. Discussion

The results verify the presence of H, Ar, C and O in the sputtered layer, with H around 5 and argon close to 8 at. %., the latter being in excess of 2% quoted in other authors' work [25, 26]. This is not entirely unexpected in the present studies because of the relatively low sputtering pressure, leading to high incorporation of reflected neutrals. The presence of H, O and C is also to be expected as contaminants from the vacuum environment during sputtering. It is worth noting that Honer and Kovacs [27], also found evidence of oxidation in magnetron sputtered silicon films. The analysis (Table 2) shows that throughout the body of the film and with the possible exception of H at the maximum power density examined, laser annealing does not remove the entrapped gases. However, figure 2 shows a definite argon depletion close to the surface and it is possible that this occurred with lower power densities but could not be resolved by the techniques used. Mass spectrometry showed, except for the non-annealed case, that heating small samples to 750^0C does not lead to any measurable desorption of these gases. A number of alternative reasons for the effectiveness of laser annealing in removing the problem of gas desorption during wafer bond annealing are suggested by the results. Sealing the wafer surface is one possibility, and TEM (Figure 1) shows quite clear surface changes suggestive of melting, even at low laser power densities. An estimate of the temperatures reached at the surface during annealing can be made by simulation [28]. The main uncertainties exist for the parameters of the thermal conductivity, K and the optical absorption coefficient, α. The studies of Wood et al. [29] suggests that K would lie in the range 5 to 30 mW cm^{-1} K^{-1}. α is particularly difficult to estimate, and one can expect its value to be dependent on the film deposition parameters and distance from the surface [30]. The most recent study of α under similar experimental conditions for sputtered silicon films [31] suggests this would be significantly greater than 10^5 cm^{-1} at 248 nm and

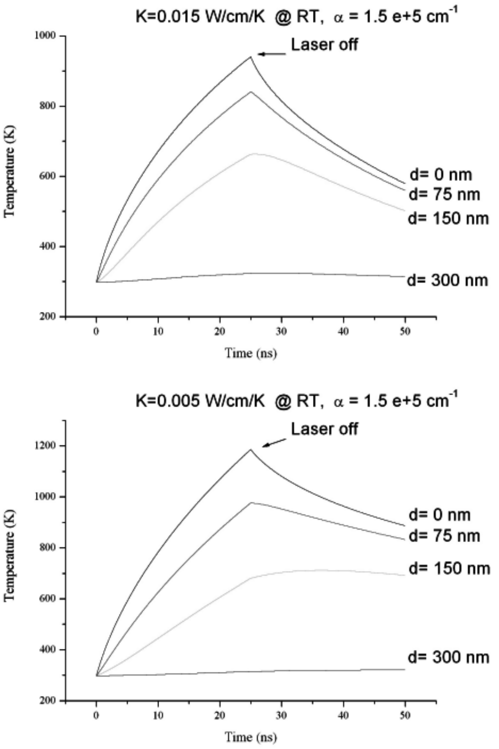

Fig. 3(a) Numerical simulation of heating from a single 30 mJ/cm^2 excimer laser pulse for two values of the thermal conductivity, K and absorption coefficient, α, = 1.5×10^5 cm^{-1}. d is the distance from the surface of the amorphous silicon film.

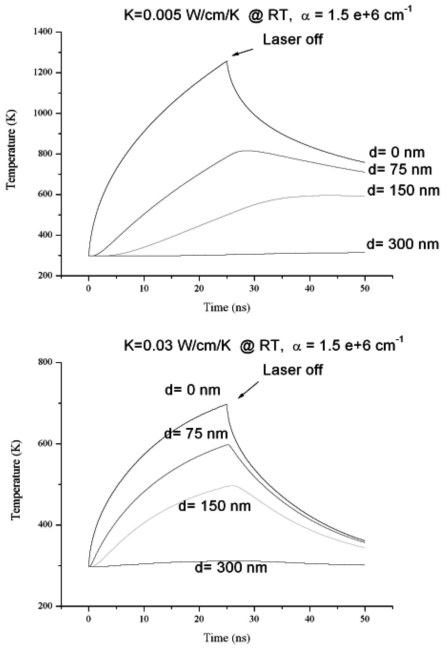

Fig. 3(b) Numerical simulation of heating from a single 30 mJ/cm^2 excimer laser pulse for two values of the thermal conductivity, K and absorption coefficient, α, = 1.5 $\times 10^6$ cm^{-1}. d is the distance from the surface of the amorphous silicon film.

Wood et al. [29] estimate a value in excess of 10^6 cm^{-1} for their modelling studies. Our current numerical simulation covers these ranges (Figure 3) and shows that for low K one may expect surface temperatures around 1300^{0}K, the melting point of a-silicon [32] and as observed in Figure 1. High values of α increase the temperature gradient at the surface, so that the lower layers are relatively less heated. In addition to surface melting, the possibility of surface oxidation needs to be considered. The vacuum during laser annealing is about 10^{-4} mbar and residual background gases would undoubtedly produce a degree of oxidation with the temperatures expected at the immediate surface. Evidence for this was revealed by EBS for the highest power density examined (sample 6). One could justifiably assume that such surface oxidation could contribute to surface sealing, although probably not as a main factor.

Depletion of gas at the immediate surface cannot be ruled out as the reason for the effectiveness of laser pulse annealing in preventing gas accumulation at the bond interface during bond-anneal of wafer pairs. However, the present results would suggest that if this is the case, then the amounts of gas involved are quite small. Previous work using acoustic microscopy showed quite clearly the random and statistical nature of gas desorption, both with respect to temperature and spatial location [17].

The present mass spectrometry experiments are limited in sensitivity by background gases, but the presence of a single spike of argon at some critical temperature, in this case 650^{0}C, supports the earlier finding; gas can desorb from one or more small or larger areas from any point on a wafer surface, at any temperature between 300 and 1000^{0}C. This could be because of randomly distributed weak points on the wafer surface or uneven distribution of gas below the surface. It is expected that during sputter deposition, argon would be incorporated into the film in a more or less uniform way, residing in shallow traps in the porous silicon network containing many dangling bonds. However, on annealing there is some evidence that bubbles could form in favourable locations. Argon bombardment of silicon or aluminium at energies in the range a few hundred eV to several keV has been found to produce bubbles, or blisters penetrating the surface when these materials are annealed at several hundred degrees Centigrade [33-37]. Argon plasma treatment of silicon for wafer-bonding has also been reported as producing bubbles penetrating the surface and causing voids during bond annealing [38]. Further, in some cases such bubbles can exist at pressures higher than equilibrium required by considerations of surface tension [37]. For a concentration of argon of 8% (RBS result, Table1), the average argon density in the film is about 4×10^{21} cm^{-3}, corresponding to about 10^{17} argon atoms in the sample compared to ~ 5×10^{14} (as estimated from the system parameters) released in the argon burst, (Figure 2). The latter corresponds to the amount of argon in about 30% of a single surface layer of the sample. Although some slow out-diffusion of gas would be expected with increasing annealing temperature, it is unlikely this would be detected by the mass spectrometry system. The burst of gas observed suggests rather a coagulation of bubbles just below the surface, in addition to any slow out-diffusion. Further investigation using TEM could show whether bubble formation occurs during the annealing process.

5. Conclusions

Low power laser annealing of the surface of sputtered silicon is effective in suppressing subsequent out-diffusion of gases trapped in the matrix of the film during sputtering. The evidence from the results is not entirely clear as to whether sealing of the surface with possible melting and oxidation is the main factor involved, or whether the annealing process simply removes gas trapped at or just below the immediate surface. Whichever is dominant, it is thought likely that coagulation of argon into bubbles could occur, building up a localised pressure, which for non-treated surfaces may lead to destruction of the bond between the two wafer substrates. The results have practical implications for the use of sputtered silicon as a bonding layer for transfer of thin films and circuitry to miscellaneous substrates.

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