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Composite Microhardness of Quartz – Al Structures

The microhardness-depth profiles of as-obtained and annealed quartz (substrate)-Al (film) structures have been investigated. A layer of constant hardness has been detected beneath the initial interface. This is supposed to result from incorporation of aluminium atoms into the surface layer of the substrate, reduction of SiO_2 and diffusion of the atoms of a certain element during the processes of preparing and rapid thermal annealing of the structures.

Keywords: microhardness, Vickers, Knoop, quartz-Al structures, Al-films, thermal annealing

1. Introduction

Aluminium films are largely applied in micro- and acoustoelectronics as components of heterostructures with various substrates. The preparation and use of quartz-Al structures have to be in conformity with possible interactions between the two materials.

It is known (THUN and VAJDA) that rapid diffusion of Al in SiO_2 is observed at $T \geq 660^{o}C$. According to Kurnosov, when semiconductor materials are doped with aluminium, a decrease in its partial pressure is observed resulting from intensive diffusion into the walls of the quartz ampoules. According to KATZ, atoms of Ga or Al diffuse easily through SiO_2 dielectric layers, in contrast to B. Consequently, SiO_2 cannot be used as masking material for selective diffusion of Al or Ga in Si wafers.

It is also known that the strong adhesion of Al to glass increases with time which is attributed to migration of oxygen to the interface and formation of an extensive reaction zone (MATTOX). BLATTNER and BRAUNDMEIER have found that at $510^{o}C$, SiO_2 in the presence of Al is reduced to Si by the formation of the thermodynamically favoured Al_2O_3. STRAUSSER et al have also found that the interface layer between sputter-deposited aluminium films and SiO_2 substrates consists of free aluminium, Al_2O_3, free silicon and SiO_2.

We are at present involved in complex studies of the specific characteristics of quartz-Al structures which result from the given regimes of preparation and annealing. Microhardness measurements are included as they may help to establish the physical location of heterophase components in multiphase structures (BALEVA et al). As reviewed by BÜCKLE, microhardness testing, in combination with other techniques, has now become almost a routine method of studying diffusion phenomena, coring, solid solubility, etc.

2. Samples

Aluminium films with thickness of 120 nm were deposited by magnetron sputtering on mechanically polished monocrystalline quartz substrates. Rapid thermal annealing (RTA) of the structures was carried out in vacuum, the temperature of the heater being 700 or 800°C. The duration of RTA ranged from 5 to 180 s. Details of the upper procedures were given by LASAROVA et al. Uncoated quartz substrates were also studied, before and after RTA.

3. Microhardness measurements

Microhardness was measured at room temperature using the PMT-3 tester (GORYUNOVA et al.) equipped with indenters of Vickers and Knoop. The pyramid was applied to the top surface of the Al layer and the contact time was 15 s each time. Test loads L ranged from 7 mN to 2 N. At a given L, at least five indentations were produced and the mean arithmetic values of the measured diagonals d were taken as experimental data. The penetration depth was h = d/7 with the Vickers indenter and h = d/30.51 with the Knoop one.

As the aluminium film was thin and the tip of the indenter penetrated through it already at L = 7 mN, the measured composite value resulted from the microhardnesses of both the layer and the substrate of the structure. For a similar pair of a soft film (Au) deposited on a hard substrate (Si), WAGENDRISTEL et al. show that the contribution of the coating results from two main effects: *i)* the imprint's diagonal is enlarged with respect to that in the substrate and *ii)* the load is distributed between the film and the substrate, thus reducing the force applied to the substrate.

4. Experimental results and discussion

Microhardness H versus penetration depth h of the Vickers indenter for four uncoated quartz substrates is given in Fig. 1. It can be seen that H of the unannealed and of the RTA-treated samples is higher at smaller h which may be connected with damage of the surface layer induced by mechanical polishing. Obviously, this effect is decreased by RTA as the highest H refers to the unannealed sample. In all cases H decreases with growing of h; at h ≥ 1.4 µm it tends to become independent of h (and L). These bulk microhardness values lay in the interval (13±2) GPa and are identical with the known for SiO_2 (GILMAN).

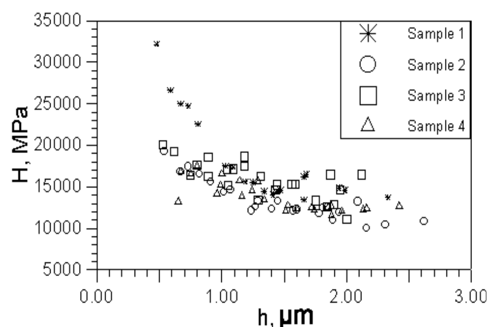

Fig. 1. H vs. h for unannealed (sample 1) and RTA-treated at 800°C quartz substrates for 15 s (sample 2), 60 s (sample 3) and 180 s (sample 4)

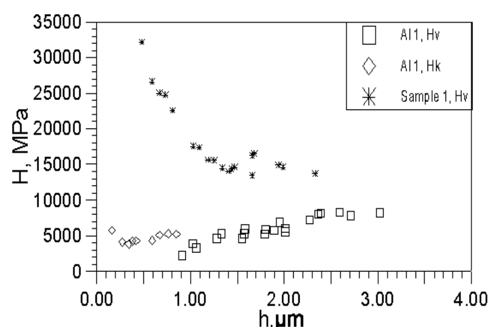

Fig. 2. H vs. h for unannealed quartz-Al structure (Al1) and quartz substrate (sample 1)

The microhardness-depth profiles of an unannealed quartz-Al structure and of substrate sample 1 are compared in Fig. 2. Because of its shallower penetration depth, the Knoop pyramid was also applied to the testing of the structure. It can be seen that the soft aluminium film not only decreases considerably the composite microhardness (compared with H of the uncovered substrate) but also changes the type of the dependence of H on h: H increases with increasing of h. This is characteristic for structures consisting of a hard substrate and a softer film. The composite Hv tends to reach saturation (about 8.3 GPa) at $h \geq 2.2$ µm ($L \geq 1.2$ N). As one can see, the values taken with the pyramid of Knoop (Hk) form a plateau (about 5 GPa) at h<1µm.

The H - h profiles of two RTA-treated for 5 s quartz-Al structures are given in Fig. 3. It can be seen that H tends to saturation at approximately the same h as for Al1 - around 2.0-2.3 µm. It is also seen that the data taken with the Knoop indenter form well-defined plateaus (about 5.3 GPa) at h = (0.8-1.3) µm.

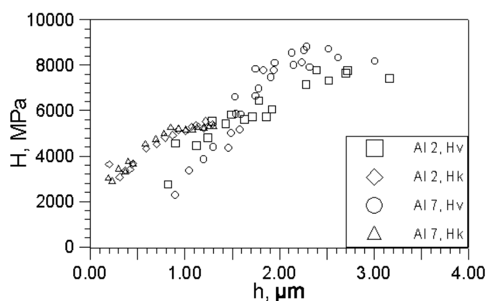

Fig. 3. H vs. h for two RTA-treated for 5 s quartz-Al structures (Al2 at 700°C and Al7 at 800°C)

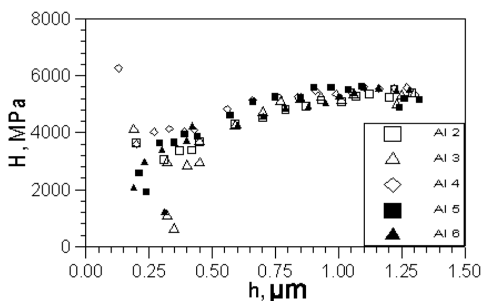

Fig. 4. Hk vs. h for five RTA-treated at 700°C quartz-Al structures (Al2 for 5 s, Al3 for 15 s, Al4 for 30 s, Al5 for 60 s and Al6 for 180 s)

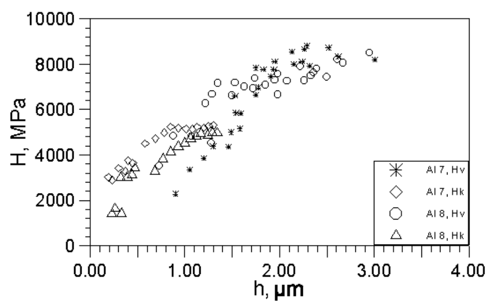

Fig. 5. H vs. h for two RTA-treated at 800° C quartz-Al structures (Al7 for 5 s and Al8 for 60 s)

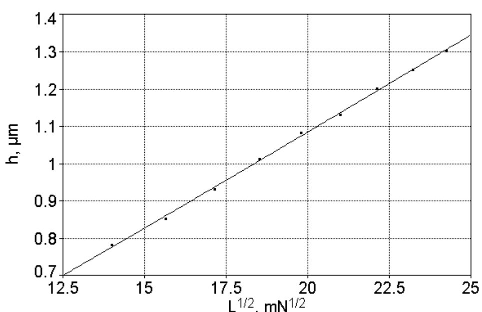

Fig. 6. h vs. $L^{1/2}$ for Al7

Plateaus at 4.9-5.5 GPa were detected in the Hk - h profiles of all the annealed at 700°C or 800°C quartz-Al structures (Figs. 4 and 5).

In order to prove that the observed plateaus are not connected with complete "spreading" of the load by the soft aluminium film, we have replotted our experimental data in depth/(load)$^{1/2}$ curves. The obtained straight lines (an example is given in Fig. 6) are an

indication of constant hardness, the latter being inversely proportional to the square of the gradient. Provided the soft film "spreads" the test load completely, a decrease of the gradient should be observed at a certain depth; when the indenter finally penetrates further into the substrate, the gradient should increase. Such a behaviour has been predicted by theory and proved experimentally for thin gold films on glass substrates (POLLOCK et al).

The upper results prove that the layers located from ~ 0.8 to 1.3 μm beneath the top surface (and the initial interface) of the quartz-Al structures are of constant microhardness. Such layers have not been detected at the given depth in the uncoated quartz substrates, before or after RTA.

The layers of constant microhardness obviously result from the incorporation of high-energy aluminium atoms into the surface layer of the quartz substrate during the process of magnetron sputtering. After this, especially during RTA, reduction of SiO_2 by Al is to be expected. The complex chemical composition of the newly formed interface layer is obviously the cause for the measured microhardness values in the plateaus (around 5 GPa), which do not correspond to the microhardness of any of the involved substances (Al, Si, Al_2O_3, SiO_2). These findings are in accordance with the cited references with the exception of the interface layer thickness.

For the case of sputtered aluminium atoms (no thermal annealing reported) STRAUSSER et al find that the reaction products are distributed over a layer approximately 400 Å thick; according to BLATTNER and BRAUNDMEIER, 0.3 μm of SiO_2 are completely converted by thermal treating for about 1000 h. These small thicknesses make us to believe that in our case of magnetron sputtering, followed by RTA for duration which does not exceed 180 s, the newly formed 0.5 μm thick layer of constant microhardness results from two effects. The second one may be diffusion of the atoms of a certain element(s), initially present in the structure, or liberated by the reduction reaction. At higher temperature and/or longer duration of RTA these atoms may be dispersed to greater depths causing a decrease of the length of the plateau x: in the case of RTA for 60 s x is smaller than that for 5 s, at the same annealing temperature (Fig. 5). The latter behaviour corresponds to diffusion from a limited source.

Assuming that x is the diffusion length, from the equation:

$$x = (D\ t)^{1/2},$$

where t is the duration of RTA, we have evaluated the diffusion coefficient of these atoms in quartz at 700 - 800°C: $D = 5x10^{-10} - 1.4x10^{-11}$ cm^2/s. These values are quite reasonable compared with the known diffusion coefficients at 900°C in SiO_2 of gallium ($D = 1.3x10^{-13}$ cm^2/s), which is accepted to be similar to that of aluminium, and of oxygen ($D = 2.8x10^{-9}$ cm^2/s) (TSAI).

The results from our microhardness measurements will be further interpreted in combination with the data from other analyses which are now in progress and will be presented in another paper.

Conclusion

A layer of constant microhardness is formed in the studied quartz-Al structures, beneath the initial interface. This is presumably associated with incorporation of aluminium atoms into the quartz substrate, followed by reduction of SiO_2 and diffusion of the atoms of a certain element during the processes of film deposition and RTA of the structures.

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