A preliminary evaluation of the potential of laser-beam heating for the production of high melting-point oxide coatings

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Laser evaporation *in vacuo* has been used to prepare ceramic coatings on single-crystal silicon wafers from sintered Mg_2SiO_4 targets. The morphology of the coatings resembles that of other coatings prepared by arc-source ion plating, while preliminary secondary ion mass spectrometry (SIMS) analysis indicates that the coatings have a higher silicon content relative to the target material.

1. Introduction

The introduction of commercial physical vapour deposition (PVD) techniques such as ion plating [1] and sputtering [2] has created a lot of interest in producing hard ceramic coatings (especially TiN) at low temperature. However, the range of compounds which can be produced by these techniques remains mainly restricted to two component systems. Furthermore, the production of oxide coatings, by r.f. sputtering, or electron beam evaporation, is often problematic and deposition rates by the former method are very slow [3].

In the present investigation, a novel method of producing high melting-point, complex, oxide coatings was sought, which was both rapid and reproducible. The technique was required for the production of thin Mg_2SiO_4 layers on silicon wafers for diffusion couple experiments. Early attempts to produce Co_2SiO_4 coatings via r.f. sputtering, using hot-pressed targets, proved unsatisfactory since target preparation was costly (in view of the large size required; $\gtrsim 50$ mm diameter), deposition rates were very slow (1 to 3 nm min^{-1}) and the surface finish of the resultant coatings was inadequate [4]. Recent experiments [5] using a 500 W Nd-YAG laser revealed that sufficient surface heating can be provided by laser excitation to cause a $\sim 5\,\mu$m layer of TiC, TiN or Al_2O_3 to be completely evaporated, by one laser pass, under optimal conditions. Hence, it appeared feasible to utilize this phenomenon as a means of producing refractory oxide coatings.

2. Experimental procedure

The experimental "laser evaporation" coating facility is schematically depicted in Fig. 1. The Mg_2SiO_4 targets were prepared from powder (particle size $< 60\,\mu$m), pressed at 60 N mm^{-2}, and sintered twice at 1750° C for 5 h. The targets measured ~ 9.5 mm diameter × 7.0 mm, and were held in position within the chamber by "silver dag". The polished silicon single-crystal wafer substrates were held in position by an aluminium alloy clamp, which could be adjusted to vary the substrate–target distance. For the experiments reported here, this distance was approximately 15 mm. The laser was focused on expendable target material, at normal atmospheric pressure. Focusing was judged to be optimized when the largest visible plasma was produced above the sample surface. The CNC (Computerized Numerical Control) of the Nd-YAG laser was programmed to scan a 4 mm square area. The beam diameter was 0.1 mm and the increment between laser tracks was 0.05 mm. The pulsed power mode of the laser was selected (2 kW) with a pulse period of $10^3\,\mu$sec.

Evaporation coatings were produced by evacuating the chamber to better than 10^{-5} mbar (1 mPa), using the rotary/turbo-molecular pumping group, and making the laser scan the target surface, typically 50

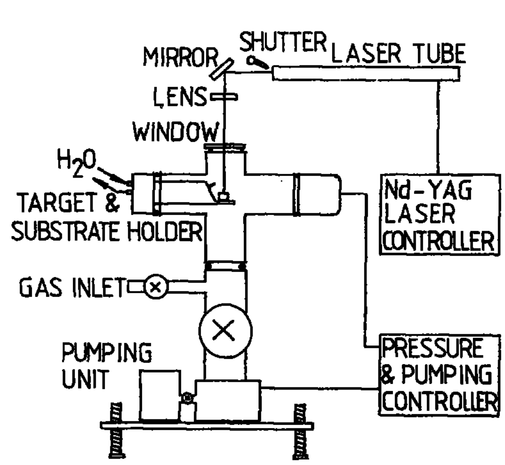

Figure 1 Schematic depiction of laser evaporation unit.

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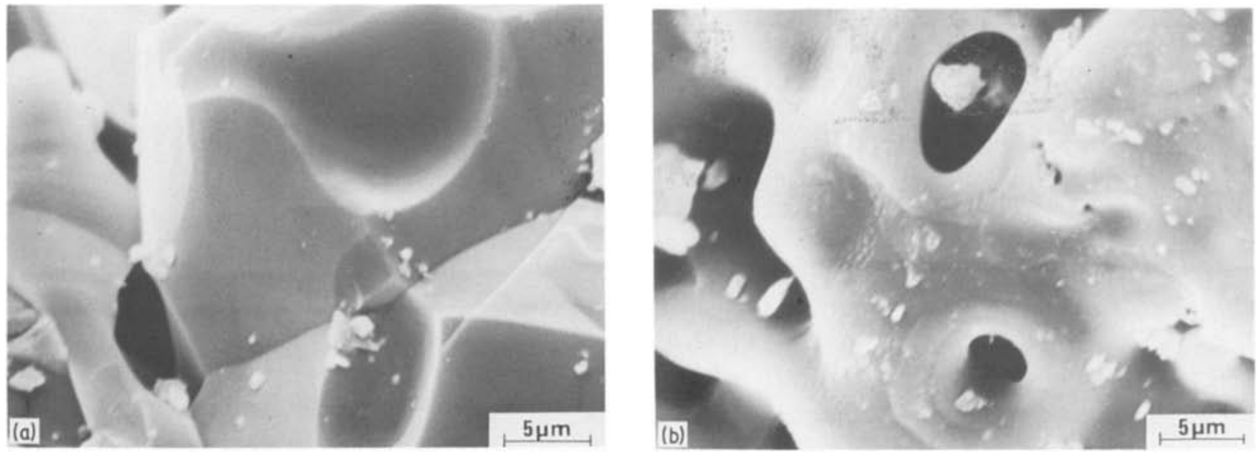

Figure 2 Surface of Mg_2SiO_4 target: (a) original surface; (b) laser-melted surface.

times. The water cooling of the substrate holder ensured a constant substrate temperature.

3. Results

Coatings $\sim 0.5\,\mu m$ thick were produced after the laser was traversed 50 times over the target surface, causing approximately $32\,mm^3$ of material to be evaporated.

Examination of the lasered target surface revealed evidence of melting (Fig. 2), the original grains being smoothed considerably. Fine debris $6\,\mu m$ across was also scattered across both the lasered target surface and the target surface lying directly adjacent to the lasered zone.

All the coatings had a very similar appearance, comprising fine near hemispherical asperities, ranging in size from 0.1 to $8.0\,\mu m$ across. Many of the larger hemispheres were noticeably flattened, while others had a "doughnut" appearance (Fig. 3). There were also areas, up to $20\,\mu m$ across, where the coating appeared to have spalled off (Zone A in Fig. 3).

The preliminary raw secondary ion mass spectrometry (SIMS) data (using an incident argon ion beam of ~ 0.5 mm diameter), is presented in Figs 4 and 5 and numerically in Table I. Normalization of the raw data reveals that the oxide coating is enriched in silicon (Table II), while the relative ratios of magnesium and oxygen are commensurate with the target material.

Since the layers were only $0.5\,\mu m$ thick it was not possible to use X-ray diffraction to ascertain whether the coatings were crystalline or amorphous.

4. Discussion

The surface morphology of the coatings shown in Fig. 3 in some respects resembles that of TiN coatings produced by reactive ion plating utilizing an arc source (Fig. 6), although the number of hemispherical asperites is somewhat less, and no doughnut-like asperities are observed in the latter case.

From the appearance of the coating surface it seems that evaporation of the target, via laser heating, proceeds via the formation of a mixture of vapour and liquid, whereby a fine spray or aerosol of matter is ejected from the target surface. Indeed an early hypothesis advanced by Ready [6] suggested that the subsurface of materials during laser excitation becomes superheated and reaches the heat of vaporization before the surface, resulting in the eruption of plumes of matter analogous to a thermal explosion, presumably because the surface itself reflects a large quantity of the incident laser light and heat. Hence, much of the matter ejected from the target surface may contain discrete pockets of vapour, which erupt upon impacting the silicon substrate surface, producing the observed doughnut-like features (Fig. 3).

The SIMS analysis indicated that the layers produced by the laser evaporation technique are enriched in silicon. It remains unclear whether this is a reflection of a difference in the rate of mass transport of the constituent target elements in the vapour phase, or whether in fact discrete quantities of substrate are dissolved by the fine aerosol of liquefied target material prior to solidification on the silicon substrate.

TABLE I Raw SIMS data

	Distance from surface (nm)	Secondary ion intensity (total counts)		
		Mg	Si	O
Standard	250	40 000	10 000	45
	500	64 000	7 000	50
	750	72 000	7 000	50
	1000	75 000	7 000	50
Layer	250	27 000	7 500	18
	500	7 000	1 500	5
	750	4 000	1 000	3
	1000	3 000	1 000	3

TABLE II SIMS data normalized relative to oxygen secondary ion counts

	Distance from surface (nm)	Normalized secondary ion intensities		
		Mg	Si	O
Standard	250	890	214	1
	500	1282	139	1
	750	1440	140	1
	1000	1494	140	1
Layer	250	1540	434	1
	500	1402	300	1
	750	1332	333	1
	1000	1000	333	1

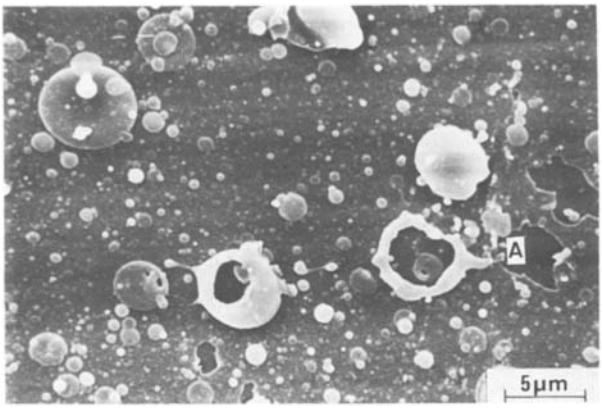

Figure 3 Oxide coating produced on silicon substrate. Note doughnut features and area of decohesion (A).

It has not yet been possible to determine the crystallography of the coatings but it appears probable from the earlier work of Ban and Kramer [7] that they are likely to be amorphous or at least microcrystalline.

The utilization of the Nd-YAG laser in the present work was found to be particularly useful since it was very easy to accurately control the surface area of the target being scanned. It is believed that this approach

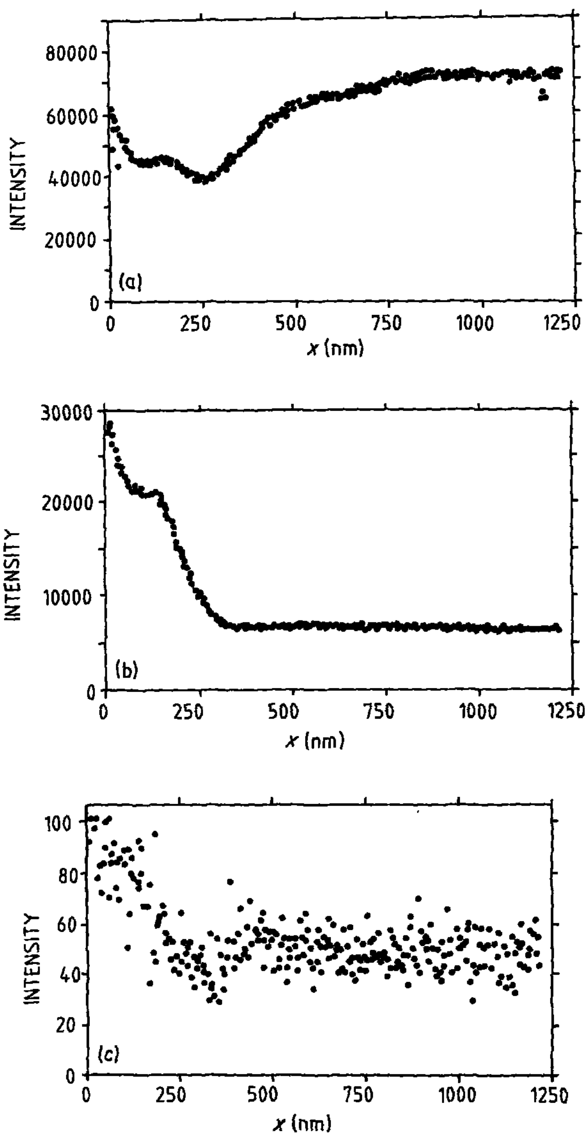

Figure 4 SIMS concentration profile of Mg_2SiO_4 target showing distribution of (a) Mg (b) Si (c) O.

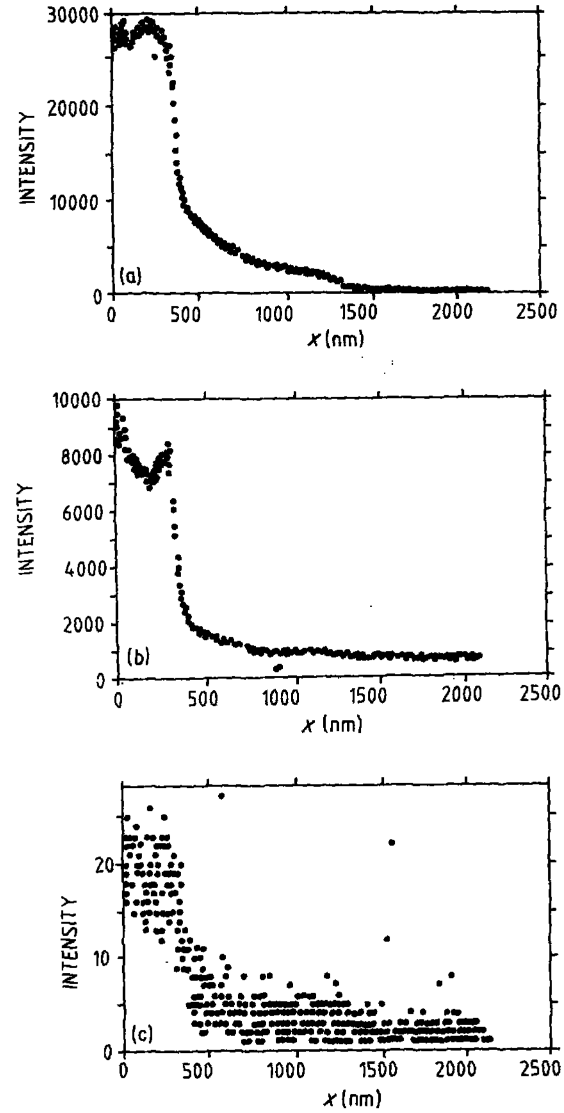

Figure 5 SIMS concentration profile of oxide coating showing distribution of: (a) Mg, (b) Si, (c) O.

may have potential use in the commercial sector for the production of evaporation coatings. In particular, laser-beam heating could prove to be a powerful method of evaporating target materials in the ion-plating technique, since existing techniques of arc or electron-beam heating have a number of disadvantages which are obviated by using a laser. For example, arc evaporation is random and does not ensure a uniform

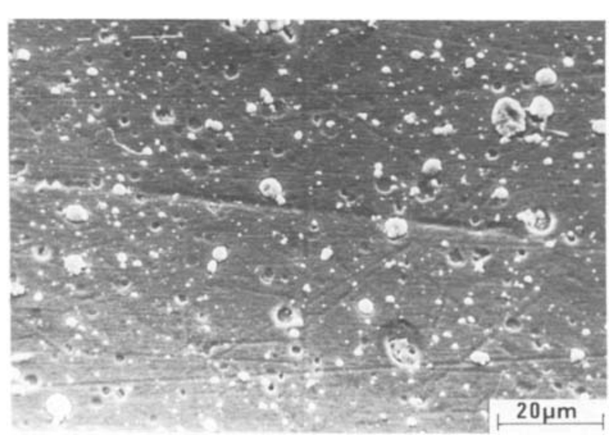

Figure 6 TiN coating deposited on a Ti–6Al–4V substrate by arc-source reactive ion plating.

rate of target consumption, and both arc and electron-beam evaporation are sensitive to working pressure, whereas laser evaporation allows uniform erosion of the target, is less sensitive to working pressure and simpler target geometries can be used. Furthermore, both arc and electron-beam sources cannot be operated efficiently if the target is a dielectric or insulator, whereas laser interaction with a surface is insensitive to the electrical conductivity of the target.

5. Conclusions

1. An Nd-YAG laser has been successfully utilized for the production of 0.5 μm oxide coatings on silicon single-crystal wafers *in vacuo*.

2. Preliminary SIMS analysis indicates that the coatings are enriched in silicon, while the magnesium and oxygen content is commensurate with the Mg_2SiO_4 target. It has not yet been possible to determine the crystallography of the coatings.

3. Laser "evaporation" of the target appears to involve the formation of both gaseous and liquid phases, the latter being transported in the form of an aerosol of discrete droplets.

4. The laser evaporation principle appears to hold significant future commercial potential, especially in the field of ion plating.

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