Nuclear Instruments and Methods in Physics Research B9 (1985) 20–24
North-Holland, Amsterdam

TWO TYPES OF MeV ION BEAM ENHANCED ADHESION FOR Au FILMS ON SiO_2 †

C.R. WIE, C.R. SHI *, M.H. MENDENHALL, R.P. LIVI **, T. VREELAND, Jr. ***
and T.A. TOMBRELLO

Division of Physics, Mathematics, and Astronomy, California Institute of Technology, Pasadena, California 91125, USA

Received 26 June 1984 and in revised form 28 October 1984

The ion beam-enhanced adhesion of thin Au films on vitreous silica substrates was studied for a wide range of Cl ion beam doses for beam energies between 6.5 MeV and 21.0 MeV. Since the residual adhesion of Au on SiO_2 is low, the improved adhesion can be easily seen using the Scotch Tape Test. The threshold in the enhanced adhesion corresponding to passing the tape test occurs at two different dose ranges for a given energy; one at very low dose centered around 1×10^{13} /cm^2, the other at higher doses with a threshold of around 1.5×10^{14}/cm^2 (depending upon the beam energy). At low doses (2×10^{12} to 5×10^{13}/cm^2) surface cracks occur on the SiO_2 substrates, these cracks close up at doses higher than 5×10^{13}/cm^2. A possible explanation of enhanced adhesion in the low dose range is associated with the surface crazing of the SiO_2 substrate. To make the adhesion test more quantitative, a scratch test was also used on the samples.

1. Introduction

Adhesion improvement of various thin metal film–substrate combinations by high energy ion beam irradiation has been studied by various groups [1]. The mechanism which is responsible for the increased interfacial bonding is not yet clear, and partially reflects the difficulty in measuring adhesion quantitatively and reproducibly. The enhanced adhesion mechanism for metal–metal and metal–dielectric combinations may correspond to different processes for ion energies in the electronic stopping region (MeV/amu). For metal films on dielectrics, one might expect the coupling of energy deposited in electronic excitation of substrate material into lattice displacement, resulting in atomic mixing at the interface. For metal on metal, the energy may go into interfacial bonding. Mendenhall and co-workers have shown that the atomic mixing at the interface of a thin metal film and semiconductor substrate induced by MeV ion irradiation is less than 20 Å [1]. For metal on dielectric, the mixed layer is less than 15 Å (e.g., W or Mo on Al_2O_3) [2]. This mixed layer thickness limit is very small compared to the case of low energy ion mixing or ion implantation. Thus, one can argue that the mechanism of improved interfacial bonding induced by MeV ion irradiation is different from that induced by low energy ion mixing. It is more likely that the ionization and electronic excitation by the incoming ion makes the target atoms chemically active so that it may form a suitable local environment for hot chemistry.

The vitreous fused SiO_2 substrate is an interesting target for the study of the high energy ion beam irradiation effects because of the presence of an ionization induced compaction which can lead to surface crazing [4]. The microcracks on the SiO_2 substrates induced by the ion irradiation seem to increase the thin film adhesion on the substrate even at very low dose ranges (2×10^{12} to 5×10^{13}/cm^2).

2. Experimental procedure

The substrate of vitreous fused SiO_2 was cleaned by the following steps: ~ 10 min in hot water with Alconox detergent in an ultrasonic bath; rinse in deionized water; ~ 20 min in boiling concentrated $HNO_3 : N_2O = 1:1$; rinse in methanol or deionized water. We changed from methanol to deionized water in the last step in the cleaning procedure to see if that causes any notable difference in the adhesion threshold; however, no marked difference was observed. The cleaned SiO_2 substrate was coated (resistively evaporated) with about 350 Å of Au in a vacuum of 2×10^{-6} Torr. The samples were bombarded with a Cl beam to various doses at different energies with the Caltech EN tandem accelera-

† Supported in part by the National Science Foundation (DMR-8318274).

* Permanent address: Nuclear Research Institute, Lanzhou University, China.

** Permanent address: Instituto de Fisica-UFRGS-90000, Porto Alegre, Brazil. (Fellowship from CNPq-Brazil.).

*** Permanent address: Division of Engineering and Applied Science, Caltech., Pasadena, CA 91125, USA.

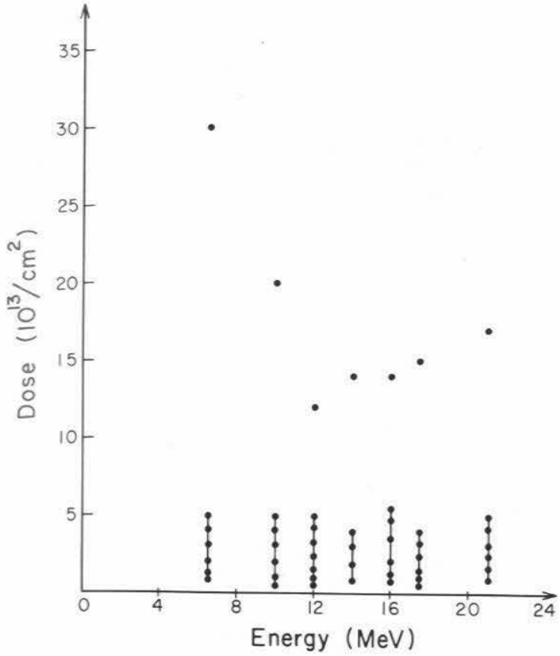

Fig. 1. Threshold dose versus Cl bombarding energy for Au films on SiO_2. The bars for doses less than $5\times10^{13}/cm^2$ represent the low dose adhesion range where beam spots pass the Scotch Tape Test. The dots represent the threshold dose for the high dose adhesion using the same test. The adhesion fails the Scotch Tape test at doses in between the high dose threshold and the largest dose (around $5\times10^{13}/cm^2$) of low dose adhesion.

tor. The beam current during irradiation was less than 65 nA/cm^2. During irradiation the target pressure was $\sim 1\times10^{-6}$ Torr, with a liquid nitrogen cooled shroud around the target to reduce the deposition of hydrocarbons. The irradiated samples were tested with Scotch Tape and the scratch test.

3. Results and discussion

The range of doses for the low dose adhesion and the threshold dose (above which all pass the Scotch Tape Test) are given as a function of energy in fig. 1. The threshold dose for high dose adhesion varies with energy approximately as expected from the variation of the electronic stopping power of the Cl beam in SiO_2 (table 1). But the range of doses for low dose adhesion (for those which pass the tape test) is approximately constant over the energy range investigated. In this dose range (from 2×10^{12} to $5\times10^{13}/cm^2$), microcracks occur on the SiO_2 surface. The typical crazed area is 100 μm across; the crack width is about 0.1 μm and has a depth of about the ion range (6.2 μm for the 15 MeV Cl ion bombarded sample) (fig. 2). For subsequent higher doses, the microcracks close up leaving only the faint traces of the cracks (fig. 3), and the irradiated surface of the SiO_2 substrate becomes smooth and shiny again. The compaction of SiO_2 under irradiation was about 3% of the ion range (1800 Å for 15 MeV Cl with range of about 6 μm). We believe that the incomplete disappearance of the microcracks is due to the imperfectly clean environment of the substrate surface. The appearance of surface crazing on vitreous silica irradiated by low energy ion beams (e.g., 103 keV Ar or 1.135 keV H) was studied by Primak and his colleagues [4]. They believed that the surface crazing is exfoliated somehow by higher dose irradiation, which does not seem consistent with our results. Since an MeV ion leaves a cylindrical damage track along its path in an insulator [3], we can think of the compaction in SiO_2 as occurring

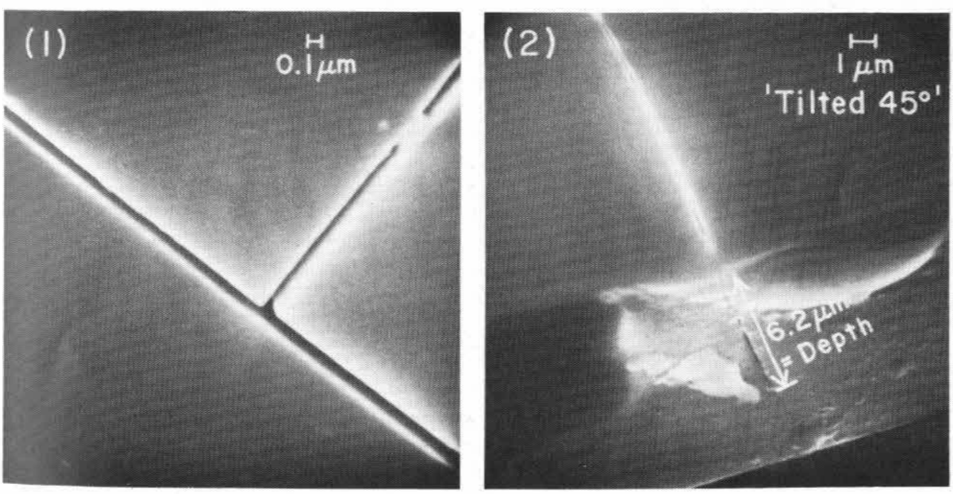

Fig. 2. These SEM pictures show (1) crack width, (2) crack depth of the 15 MeV Cl irradiated vitreous SiO_2.

in each of the cylindrical damage tracks [4]. For beam doses larger than $1/\pi r^2$, where r is the damage track radius at the surface [3], the compacted damage track regions overlap to give a laterally uniform compacted region over the whole beam spot, and the cracks close up. If we take the threshold beam dose at which the

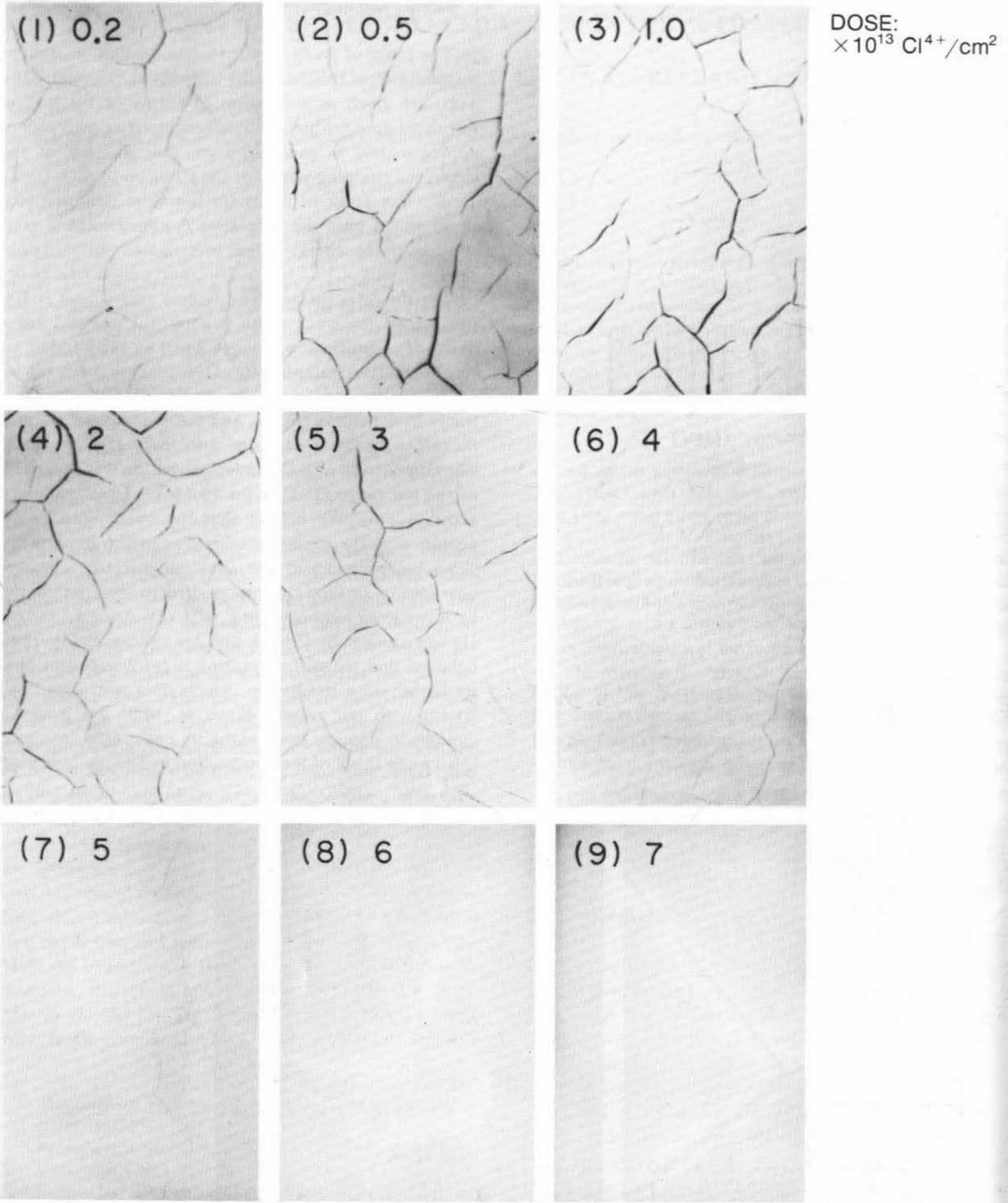

Fig. 3. Pictures from (1) to (9) show the appearance and disappearance of cracks on the vitreous SiO_2 substrates as a function of 15 MeV Cl ion beam dose (DOSE: $\times 10^{13}$ $Cl^{4+}cm^{-2}$). The dimension of the picture for each dose is 300 μm wide by 450 μm high.

Table 1
Threshold doses to pass the Scotch Tape Test are given for low and high dose enhanced adhesion. The inverse of electronic energy loss of a Cl ion in SiO_2, $(dE/dx)^{-1}$, is given for comparison.

E (MeV)	Low dose range ($\times 10^{13}/cm^2$) Min.	Max	High dose threshold ($\times 10^{13}/cm^2$)	$(dE/dx)^{-1}$ in SiO_2 $(5236\ eV/Å)^{-1}$
6.5	0.8	5	30	22.5
10	0.5	5	20	16.4
12	0.5	5	12	14.8
14	0.8	4	14	14
16	0.8	5.5	14	13.6
17.5	0.5	4	15	13.3
21	0.8	5	17	12.8

surface crazing disappears to be 6×10^{13} ions/cm^2 for 15 MeV Cl ions, r is around 7.3 Å, typical of track radii [3]. At a dose corresponding to maximum crack density ($\sim 1.5 \times 10^{13}$ ions/cm^2), the radius of a circular area per ion is about twice r, which would lead to high local stresses in the material.

The adhesion mechanism seems to be different for the two dose ranges. For the low dose range (from $5 \times 10^{12}/cm^2$ to about $5 \times 10^{13}/cm^2$), the cracks appearing on the SiO_2 substrate resulting from the non-uniform stress relaxation of ionization compaction might be responsible for the improved sticking of the Au film to the substrate. An accidental observation that an irradiated SiO_2 substrate dropped on the floor gathers fine dust particles along the cracks on the beam spots gives a clue to the relation between the thin film adhesion and the cracks on the substrate surface. For higher doses, the enhanced adhesion is the same mechanism that was observed from MeV ion irradiation of the metal film–dielectric substrate samples [1], even though the exact mechanism has not been found so far. Further study is necessary to reveal the exact mechanism involved in the enhanced adhesion in the high dose regime for Au films on SiO_2. A study using ESCA or XPS to look at the compound formed at the interface or a study using a high resolution RBS channeling or a high resolution TEM to see the interface mixing at the monolayer level may be very useful but may be beyond the sensitivity limits of these techniques. Recently a transmission channeling study which is sensitive to monolayer mixing at a metal–silicon interface was reported [5]. We believe that the low dose adhesion may be due to the high electrostatic field intensity at the edge of the microcracks (about 1000 Å width). As the microcracks close up at higher doses, this edge field also disappears giving lower overall adhesion strength to the film.

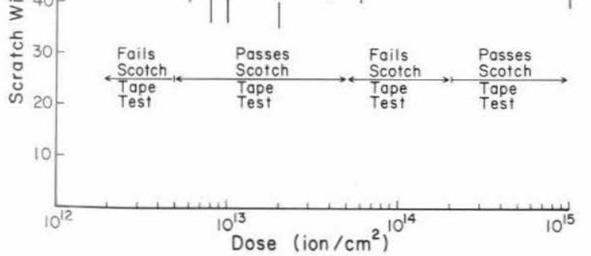

Fig. 4. Scratch width as a function of beam dose. For the dose range from $5 \times 10^{12}/cm^2$ to $5 \times 10^{13}/cm^2$, where the width shows a minimum, the beam spots pass the Scotch Tape Test. The beam spots also pass the tape test for doses higher than approximately $2 \times 10^{14}/cm^2$.

The thresholds for the higher dose adhesion vary with the ion energy approximately as expected from the variation of the stopping power of the Cl ion beam in SiO_2. The threshold values for low dose adhesion and high dose adhesion with the stopping power are given in table 1. However, a least χ^2 fitting of the high dose threshold, D_{th}, to a function of the form $(dE/dx)^{-n}$ was not successful, perhaps indicating that we either need more data points at higher energies or more terms in the functional dependence, $F(dE/dx)$.

We tried scratch tests on the same samples with a 1 mm diameter steel ball tip. The ball scratched off the Au films in the beam spots as well as the films in unirradiated area at the lowest weight we could use. However, the scratch track width, at the load of 10 g, varies with beam dose showing a minimum at the low dose enhanced adhesion range and a decreasing trend above $1 \times 10^{14}/cm^2$ (fig. 4).

These data show clearly that the phenomenon of enhanced adhesion by MeV ion bombardment may involve several distinct processes. Only the presence of a clear gap in the Scotch Tape tested samples as a function of beam dose exposed their existence in this case. One must, therefore, employ reliable and broad range adhesion tests in order to avoid inadvertent association of different adhesion mechanisms. The utility of scratch tests for such adhesion measurements has been demonstrated in this regard; further studies will be made to determine their range of applicability.

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