3-21-1994

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(Received 30 September 1993; accepted for publication 17 January 1994)

Excimer laser pulses with wavelengths of 248 and 308 nm were used to selectively seed Pd on SiO_2 surfaces, making them suitable for electroless plating. This novel seeding process for insulating materials is accomplished with the sample immersed in the seeding solution, and occurs only on the areas of the substrate that are illuminated (through the liquid) by the laser light. The Pd content of the seeded samples increased with the number of pulses, but was rather independent of repetition rate. The deposition rate showed a dependence with wavelength consistent with a defect driven mechanism for electron excitation through the band gap of SiO_2. These electrons then reduce the Pd ions in the solution in contact with the surface.

In the process of electroless plating, the reduction of the metal ion is normally initiated by a catalyst on the surface (seed). The deposition of this seed, however, is not a trivial problem, and it typically occurs on metallic surfaces due to atomic exchange. Seeding on nonmetallic substrates has in the past required the presence of an additional layer, either a metallic film, or a metalorganic film that needs further activation. In the latter case, lasers have been used to decompose photosensitive surface layers.[1-3]

Recently, another seeding mechanism, which derives from electron excitation through the band gap of the insulator by the laser light and subsequent relaxation, has been proposed.[4] This process, which depends on the energy of the laser light, the properties of the material, and equilibrium potential of the solution, has been used by other authors, assisted by a continuous Ar-ion laser, to deposit noble metals on a surface covered by a narrow band-gap TiO film.[4] With the help of excimer lasers we have taken the latter concept and extended it to any insulating surface with focus on seeding, because it can be controlled better than plating. Our process does not require pretreatment of the surfaces, and works with several standard seeding solutions normally used to seed on metals such as $PdSO_4$, $Pd(CH_3CO_2)_2$.

In a previous work we used this method to seed on polyimide surfaces.[5] In that case, the deposition of Pd increased with the number of pulses, and with pH of the solution; it was also found to be insensitive to the repetition rate. These results, as well as the dependence on fluence indicated a single photon absorption mechanism, in agreement with the photon energies of the 248 and 308 nm laser radiation (5 and 4 eV, respectively) and the absorption spectra of polyimide.[6] In this work we are addressing the laser assisted seeding on SiO_2 surfaces and we discuss why the method is successful also in the case of wide band-gap insulators.

A schematic representation of the experiment can be found in Ref. 5. The samples were irradiated while immersed ($\simeq$1 mm from the surface of the liquid) in a standard seeding solution (0.1 g/ℓ $PdSO_4$ in 0.1 *M* H_2SO_4, with and without 5% isopropyl alcohol) which exhibits negligible absorption in the ultraviolet UV region accessible with the excimer laser. The absorption values for a 1 mm path through the seeding solution were 0.105 and 0.06 for the 248 and 308 nm lines, respectively, and they did not change with the addition of 5% alcohol. After seeding, the samples were rinsed in distilled water and dried with compressed air. The dependence of Pd deposition on fluence, number of pulses, and repetition rate was assessed by x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), Rutherford backscattering spectroscopy (RBS), and atomic force microscopy (AFM).

We measured the dependence of Pd deposition on laser fluence, number of pulses, and repetition rate for both the 308 and the 248 nm lines. The deposited amount of Pd showed a strong dependence on the presence of alcohol in the solution. The alcohol, which is an electron donor, is believed to act as a hole scavenger preventing electron-hole recombination at the surface,[4] and our observations suggest the presence of a large number of surface recombination centers in SiO_2. The possibility of the laser decomposing the solution because of the alcohol was unlikely, in view of the minimal effect alcohol had on the UV absorption. As for the dependence on repetition rate, we did not find any significant difference in deposition, as expected for a process in which thermal effects are not supposed to play a role.

The differences in coverage produced by the 308 and 248 nm lines are obvious in Fig. 1, which shows AFM pictures of the seeded surfaces. Figure 1(a), which corresponds to irradiation with 308 nm light after 3000 pulses at 300 mJ/cm^2, shows a surface with isolated islands. In contrast, Fig. 1(b), which corresponds to irradiation with 248 nm light after 2000 pulses at 210 mJ/cm^2, shows extensive Pd coverage. This coverage, however, showed some variations throughout the irradiated area. Regions with lower Pd density, probably produced by variations in the local energy density across the irradiated surface, could be observed by scanning larger areas with the SEM. These measurements, made with the detector window tuned to the Pd fluorescence, were, in general, consistent with the bumps observed by the AFM. Samples such as that of Fig. 1(b) immersed for 2 min in a Co-containing electroless plating bath, plated well. In contrast, no significant plating was accomplished on samples such as that of Fig. 1(a).

The failure of metal deposition for samples such as that of Fig. 1(a) is consistent with previous observations.[7] Small isolated Pd nuclei were able to initiate electroless metal deposition only when they were beyond a certain size. This

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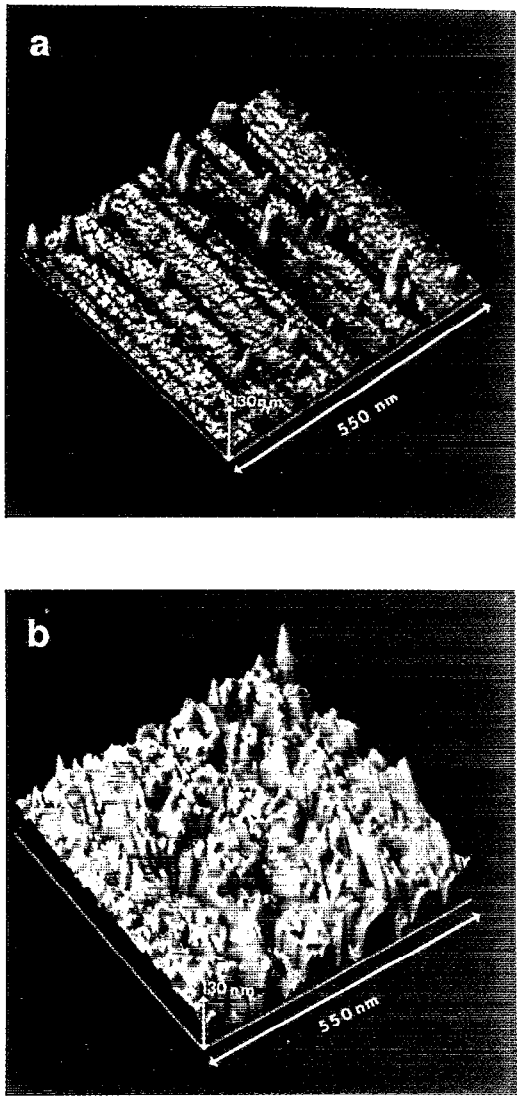

FIG. 1. AFM scans on seeded samples (a) after 3000 pulses at 300 mJ/cm^2 with the 308 nm line; (b) after 2000 pulses at 210 mJ/cm^2 with the 248 nm line. The scanned area was 550×550 nm.

effect has been attributed to nonlinear diffusion of the Pb^{+2} stabilizer contained in the electroless plating solution.[7,8]

XPS analyses of the seeded samples showed no dependence of the Pd/Si intensity ratio with the electron take off angle. This is typical of islands thicker than the detection depth (≃30 Å) corresponding to the kinetic energy of the Pd 3*d* electrons.[9] Therefore, we used the ratio of the intensities of the Pd 3*d* and Si 2*p* XPS peaks, normalized to the intensities of a thick Pd film and a SiO_2 substrate, respectively, to estimate the evolution with number of pulses of the relative Pd coverage (θ), which is the relative area occupied by the Pd islands.

Figure 2 shows the dependence of the Pd coverage on the number of pulses for the seeding with 248 and 308 nm laser wavelengths with similar fluences (300 mJ/cm^2). The coverage produced by the 308 nm light increases monotonically with the number of pulses. In contrast, for the 248 nm light, the coverage does not seem to systematically increase beyond 700 pulses. The average coverage values deduced by

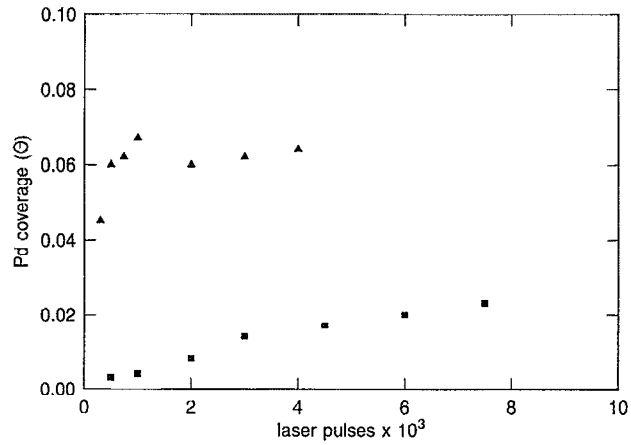

FIG. 2. Pd coverage vs number of pulses as measured by XPS. 248 nm light (triangles); 308 nm light (squares).

XPS for irradiation with the 248 nm line seem lower than that shown in Fig. 1(b). However, the coverage observed by AFM may be strongly influenced by the height of the islands and the shape of the AFM tip.

As opposed to the XPS intensity, the RBS data shown in Fig. 3 indicate increasing Pd intensity beyond 700 pulses for the 248 nm light. This suggests a regime characterized by thickening of the islands. Within this regime, however, the rate of Pd deposition exhibits a break after a number of pulses which depends on the fluence used. For 300 mJ/cm^2 (triangles), the break occurs after 700 pulses, whereas for 210 mJ/cm^2 (squares) it occurs at about 2000 pulses after achieving at this stage a higher Pd intensity than in the 300 mJ/cm^2 case. The RBS data for the 308 nm light (circles) does not exhibit a break in the slope and increases monotonically with a rate similar to that of the 248 nm light in the late stage. Figure 4 shows a comparison of the RBS spectra for samples seeded with the 248 and 308 nm light as a function of the square of the fluence. The samples irradiated with the 248 nm light are represented by dots and triangles, corre-

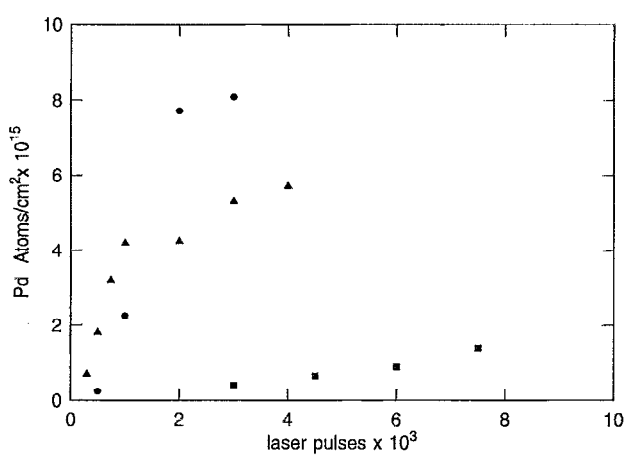

FIG. 3. Pd deposition vs number of pulses as measured by RBS. 248 nm light, 300 mJ/cm^2 (triangles) and 210 mJ/cm^2 (dots); 308 nm light, 300 mJ/cm^2 (squares).

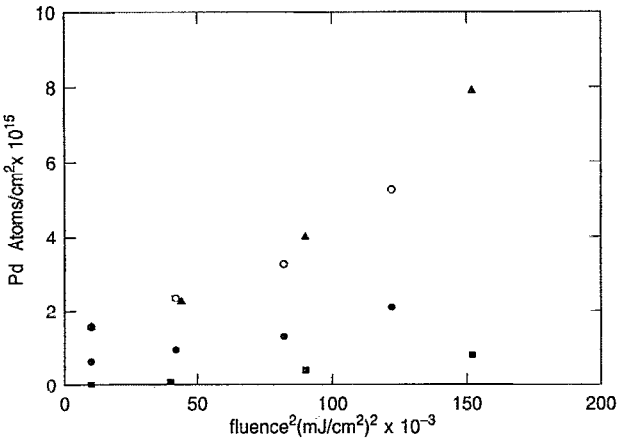

FIG. 4. Pd deposition as a function of the square of the fluence. 248 nm light, 1000 pulses (▲), 400 pulses (●), dots×2.5 (○); 308 nm light, 3000 pulses (■).

sponding to 400 and 1000 pulses, respectively. The open circles correspond to the data points represented by the dots multiplied by a factor 2.5. For these samples, the increase is not linear with the square of the fluence and the curves generated by these data points do not extrapolate to zero. These features may be indicative of more than one excitation mechanism. The Pd deposition for the samples irradiated with the 308 nm light exhibits a linear increase with the square of the fluence, indicative of an electron excitation limited by a two photon absorption process. For this case, however, the efficiency is much lower and the curve extrapolates to zero.

The difference in Pd deposition with laser wavelength seems to relate to the intrinsic mechanism of electron excitation by the laser light. For the 308 nm radiation, the photon energy is ≃4 eV, so in order to pump electrons through the band gap of SiO_2 (≃9 eV),[10] defect related energy levels in the band gap are necessary. Absorption bands at 7.6 and 5 eV due to oxygen deficient centers [ODC (I)] and [ODC (II)], respectively, have been observed.[11] The absorption intensity at 7.6 eV is 10^4 times higher than that at 5 eV.[11] However, neither band is readily accessible with the 308 line, and therefore the electron excitation through the band-gap line using the absorption associated with the 7.6 eV band as a intermediate step should be limited by a two-photon absorption process. In contrast, the 248 nm light may excite electrons to the ODC II band after a single photon absorption. In addition, a two-photon absorption may excite electrons across the band gap into the conduction bands where many absorption channels exist and the absorption is strong. Therefore, the higher deposition of Pd for the 248 line may be explained by the existence of two possible processes. A two-photon excitation process across the band gap; and a two-step, one-photon absorption process which first excites an electron to the ODC band followed by a second excitation to the conduction band by a second photon. This is different from a two photon excitation process, and is possible as long as the ODC II centers exist.

It has been shown that laser irradiation with the 248 nm light produces E' centers while the intensity of the absorption band at 5 eV decreases with number of pulses.[11] The decrease in the deposition rate observed after ≃1000 pulses is consistent with the reported decrease in the number of ODC II centers in SiO_2.[11] Once the ODC II centers become extinct, the electron excitation should be limited by a two-photon process and generate a deposition rate similar to that of the 308 line. The coexistence of these two channels, at least initially, probably determines the shape of the curves in Fig. 4 for the 248 nm line.

To further test the effect of defects on the electron excitation channels for UV absorption, we also attempted seeding on UV grade quartz. A much lower Pd coverage was observed for the 248 nm light, compared to the case of thermally grown SiO_2, while switching to the 308 nm light did not produce a Pd coverage that was significantly lower. In contrast, if the UV grade quartz was damaged by a high dose of irradiation in air with the 248 nm light, the Pd coverage attained with the 308 nm line increased with respect to that on the undamaged UV glass by a factor of 5, while the coverage attained with the 248 nm line only increased by a factor of 2. Although the nature of the defects is probably different of those described above, these results underscore the role of defects in providing absorption channels and thus electrons capable of reducing the Pd ion that reach the surface from the solution.

In summary, we have demonstrated the possibility of seeding Pd on SiO_2 by exciting electrons through the band gap to reduce the Pd ions in solution by means of excimer laser radiation. Furthermore, our results indicate that the process is possible because of the existence of an absorption band in the gap due to defect centers.

The authors wish to thank G. Coleman for the RBS measurements and A. T. Boulding for the SEM micrographs.

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