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Copper nucleation by chemical vapour deposition on organosilane treated SiO_2 surfaces

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Abstract

Self-assembled monolayers of organosilanes deposited onto SiO_2/Si substrate surfaces by either vapour-phase or wet chemical methods can act as ultrathin interfacial barriers which effectively prevent the diffusion of copper into the SiO_2 dielectric, enhance its adhesion onto it and also offer the possibility of achieving selective copper chemical vapour deposition. The initial stages of copper nucleation by chemical vapour deposition on organosilane treated SiO_2 surfaces at different substrate temperatures are investigated in detail by scanning electron and atomic force microscopy. The growth behaviour of copper clusters before coalescence is elucidated and analysed in detail. At temperatures below 190 °C nucleation occurs mostly on already formed copper clusters and coalescence is obtained due to an increase of the size of clusters in three dimensions. Above that temperature, secondary nucleation of smaller size clusters on the gaps among the larger clusters is observed, leading to coalescence almost in two dimensions. The stable clusters density initially increases with precursor injection time, passes through a maximum and then decreases, due to an increase at low temperatures of the size of clusters. An almost substrate temperature independent maximum clusters density which is obtained in the low temperatures region, indicates that nucleation of copper atoms occurs on surface defect sites which are assumed to be $Cu^{(I)}$ atoms. A low value of the apparent activation energy for nucleation, indicates higher affinity for copper chemical vapour deposition of the organosilane treated SiO_2 as compared to TiN substrates used previously. At 200 °C, coalescence following the initial nucleation period, results in continuous films with low roughness and low average height, thus leading to the practical realization of a thin yet continuous film.

Keywords: Chemical vapor deposition; Copper; Silicon oxides; Silane; Nucleation; Clusters; Scanning electron microscopy (SEM); Atomic force microscopy

1. Introduction

In the technology of sub-100 nm microelectronic devices interconnected with copper (Cu)—a reasonable alternative to more commonly used metals of tungsten (W) and aluminium (Al), due to its lower resistivity and higher electromigration resistance—the deleterious diffusion of Cu into the SiO_2

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dielectric is traditionally prevented by first depositing onto the dielectric surface, by physical vapour deposition (PVD) methods, interfacial barrier layers such as TaN, Ta, Ti, TiN or W, which also enhance interfacial adhesion [1]. Although the performance of such barriers with thicknesses of 10–30 nm has already been optimised in microelectronic applications, however such thick layers are not suitable for device fabrication with sub-100 nm features, and the materials mentioned above cannot form uniform and continuous films below 10 nm thickness, especially in high depth to width aspect ratio features. It is also not clear that the sub-5 nm thickness conformal barrier layers deposited by newly established techniques such as atomic layer deposition (ALD) are effective, due to high density of defects and fast diffusion paths such as nanopipes or grain boundaries [2].

It has been recently suggested and demonstrated [3], that self-assembled monolayers (SAMs) of organosilanes deposited onto SiO_2 by either vapour-phase or wet chemical methods can act as ultrathin interfacial barriers which increase the failure times (due to the Cu-transport-induced SiO_2 breakdown) of metal–oxide–semiconductor (MOS) capacitor structures, through an appropriate choice of the chain length of the SAM and also enhance the interfacial adhesion of Cu onto the SiO_2 through strong local chemical interaction between interfacial Cu and the terminal groups of SAMs.

In all the work done so far the Cu film was deposited onto the SAM using conventional sputtering deposition methods. However, it is obvious that in order to implement the use of SAMs of organosilanes as effective interfacial barriers between Cu and SiO_2, into the next generation of integrated circuits (ICs) having Cu interconnects with sub-100 nm dimensions, the Cu film—which may latter act as a seed layer for a subsequent Cu electrochemical deposition (ECD)—must be deposited onto the SAM monolayer by using the method of chemical vapour deposition (CVD). This is because CVD possesses the distinct advantage over PVD of producing films which are conformally uniform, i.e. they have a uniform thickness profile along the sidewalls and bottom for example of a trench (channel), thus providing a perfect step coverage with equal film thicknesses on all exposed surfaces [4]. Therefore we have undertaken a programme of work in trying to integrate the use of SAMs of organosilanes as effective interfacial barriers between Cu and SiO_2 with the metallization by Cu CVD.

From all the organosilane SAMs tested so far, the most effective as interfacial barrier between Cu and SiO_2 in MOS capacitors is the organosilane (3-mercaptopropyl)trimethoxysilane (MPTMS) [$HS–(CH_2)_3–Si–(OCH_3)_3$]. This is because it was found that the failure time due to Cu diffusion, of devices having this organosilane as a barrier, increases by almost five orders of magnitude and also the interfacial adhesion of Cu increases by at least three orders of magnitude, as compared to devices without a barrier [5,6]. We have already demonstrated that SAMs of MPTMS formed onto SiO_2 surfaces can offer the possibility of achieving selective Cu CVD, a "method" alternative to the combined processes of metallization with Cu CVD plus Cu chemical mechanical polishing (CMP) or of the Damascene process which is currently used in industrial applications [7]. The affinity for Cu CVD of the SAM surface is greatly enhanced upon UV-irradiation of the surface in air, prior to deposition. We have proposed a microscopic surface chemistry mechanism where the thiol head group (–S–H) is photo-oxidized by the ozone (O_3) which is created by the interaction of UV-light with the oxygen (O_2) in air and converted to sulfonic acid ($–SO_3^-H^+$). The sulfonic acid, due to its strong character, may interact with the (hfac)Cu(MHY) precursor molecule resulting in the creation of a strong bond between O and $Cu^{(I)}$ on the substrate surface and the substitution of Cu by H^+ in the [hfac] forming hydrogen and ionic bonds with each of the two O atoms as well as the dissociation of the [MHY] from the precursor molecule. These $Cu^{(I)}$ atoms may then act as nucleation sites (defects) for the decomposition of new precursor molecules and formation of $Cu^{(0)}$ metal thin film.

In this paper we focus in an investigation of the nucleation behaviour of Cu by CVD on UV-light irradiated SAMs of MPTMS on SiO_2 surfaces. In particular we examine in a great detail the *initial* stages of Cu nucleation, the growth behaviour of clusters and subsequent coalescence and thin film formation, at different substrate temperatures, within the two temperature regimes of CVD. Finally we analyse the effect in the Cu thin film morphological properties at different substrate temperatures of the treatment with MPTMS of the SiO_2 surfaces.

2. Experimental details

2.1. Substrates and silylation procedure

The substrates were 10×10 mm^2 square chips cleaved from device quality Si wafer with at least 100 nm thick thermally grown SiO_2 layer. They were cleaned by dipping them in sulphuric acid/sodium peroxydisulfate [$H_2SO_4/Na_2S_2O_8$] (0.5 M) solution for 15 min, washing them at least five times first with distilled and then deionised water and finally drying them in propan-2-ol vapours.

The surfaces of the substrates were treated by the method of gas phase silylation (vapour phase) [8], using MPTMS. After cleaning, the substrates were first baked for 1.5 h at 70 °C under vacuum of around 0.075 Torr in order to dehydrate their surfaces. Silylation was performed for 4 h at 100 °C. Then the valve of the silane was closed and the jar was pumped for 2 h at the same temperature, with a primary pump using a cold trap in order to effect desorption of merely physisorbed silylating molecules. This process creates SAMs of MPTMS with thickness of around 1 nm, with the methoxy headgroup [–OCH_3] strongly attached onto the substrate via siloxane bonds and the thiol tail [–SH] hanging out of the surface [9]. Immediately after silylation, the substrates were UV-light irradiated in air for 15 min by using a PenRay lamp [7].

2.2. CVD method, SEM and AFM

CVD was performed onto the irradiated surfaces by using the precursor (MHY)Cu(hfac) [2-methyl-1-hexene-3-yne Cu 1,1,1,5,5,5-hexafluoroacetylacetonate] refereed to as Gigacopper® [10, 11], in a direct liquid injection system made by TriJet™ (JIPELEC InJect). The liquid precursor contained in a glass tube was pushed by N_2 gas into an *injector* (the same used in the car engine), which opened and closed in a *pulsed* operation (2 Hz pulse frequency, 0.75 ms pulse duration), spraying liquid inside the vapourizer which was heated at around 87 °C. The vapour was transferred, by He "carrier" gas with flow rate of 90 sccm, through a glass tube which was maintained at 90 °C by a heating tape, into a glass jar reactor which lied inside an oven heated at 100 °C in order to prevent condensation of the vapour onto the jar walls. The main advantage of carrying out CVD with this system as compared to a conventional bubbler, is that it allows a precise control of the quantity of the precursor used, which depends only on the number of pulses injected, the injection frequency and the pulse duration. The possibility to control the precursor consumption is a key issue in industrial applications where the metallization process costs are important. The substrate lied on a resistively heated susceptor plate on top of a thin stainless steel plate. To investigate the Cu nucleation behaviour, cluster formation and growth, each substrate put one by one in the reactor, was exposed onto a different number of pulses at a certain constant substrate temperature. In this case of the pulsed CVD system which we use, the total precursor injection time is defined as the number of pulses multiplied by the pulse duration (0.75 ms), while the total growth time is defined as the number of pulses divided by the pulse frequency. Depositions with this precursor were performed at reactor vacuum pressure of 2 Torr. These are the optimum conditions for obtaining the maximum deposition rate [8,11,12]. A cold trap was used for the condensation of the by-products of CVD—which in this case is $Cu^{(II)}$ $(hfac)_2$—which is desorbed from the surface without decomposition at substrate temperatures below 250 °C yielding a dark blue colour solid in the trap.

After CVD, the surfaces of the substrates were examined by scanning electron microscopy (SEM) using a LEO 1530 system with GEMINI electron column. From the SEM images, the clusters density (number of clusters per unit area) and the cluster sizes were estimated versus precursor injection time at each substrate temperature, by using the software of the SEM. The surface roughness and other statistical surface parameters were determined from contact mode atomic force microscopy (AFM) measurements made onto the same substrates using a TopoMetrix scanning probe microscope with silicon rectangular cantilevers supplied by NT-MDT (Russia) [13] (cantilever dimensions: $L \times W \times T = 250 \times 35 \times 1$ μm^3, tip radius: $\sim$10 nm, cone angle: $\leqslant 22°$, resonant frequency: 20 kHz, force constant: 0.03–0.2 N/m, reflective coating: Au).

3. Results and discussion

3.1. Nucleation behaviour at the initial stages of deposition, before coalescence

The thermal decomposition of β-diketonate $Cu^{(I)}$ complexes (Gigacopper in the present case) is the first step of the disproportionation reaction by which the Cu film is eventually formed. This thermal decomposition takes place in a narrow temperature interval between 150 and 250 °C, thus we have investigated the Cu nucleation behaviour in that substrate temperature interval.

In each of Figs. 1–4, a series of representative SEM images of the surfaces of substrates after Cu CVD performed with a different number of pulses at the initial stages of nucleation, are shown, where each figure corresponds to substrates held at the same temperature of 160, 170, 180 and 200 °C respectively. A first quick look of the images (especially for substrate temperatures: 160, 170 and 180 °C, corresponding to Figs. 1–3 respectively), reveals immediately that Cu nucleation on these surfaces takes place with the formation of

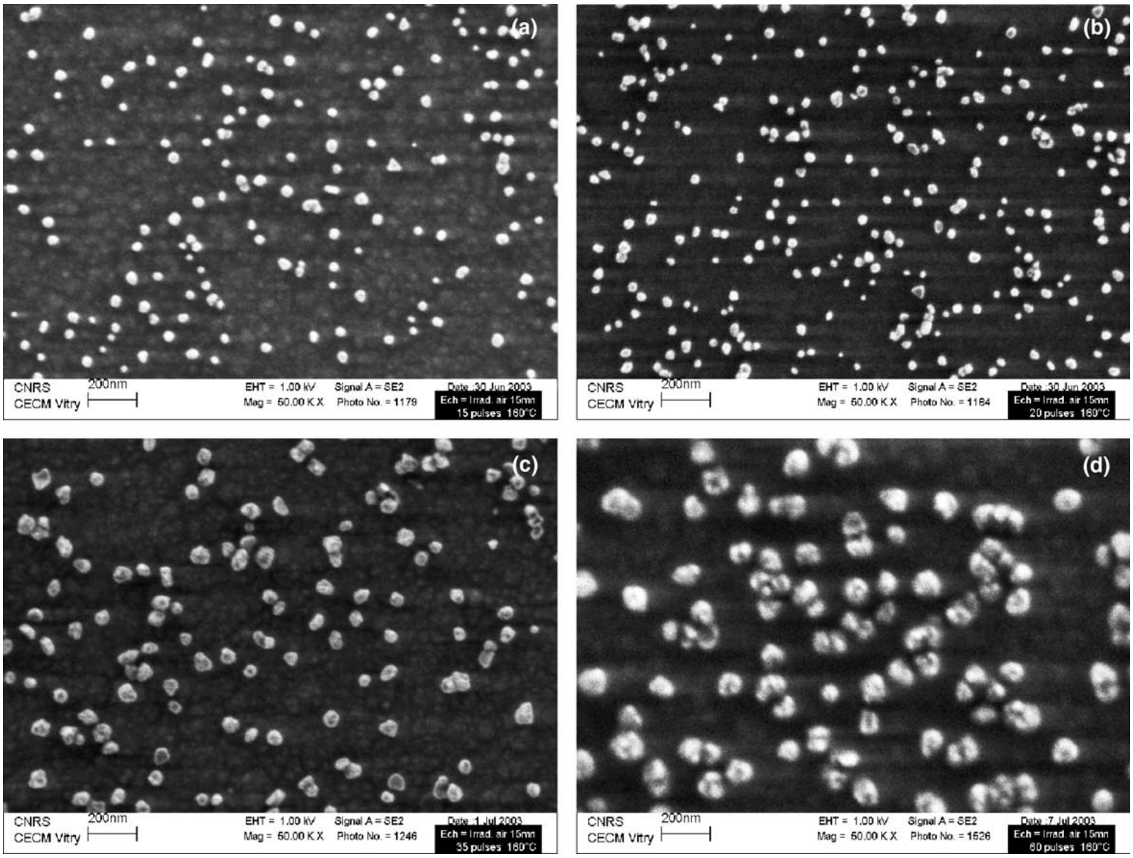

Fig. 1. Typical SEM images of the surfaces of MPTMS treated and subsequently UV-light irradiated SiO_2 substrates after Cu CVD performed at substrate temperature of 160 °C with (a) 15, (b) 20, (c) 35 and (d) 60 pulses.

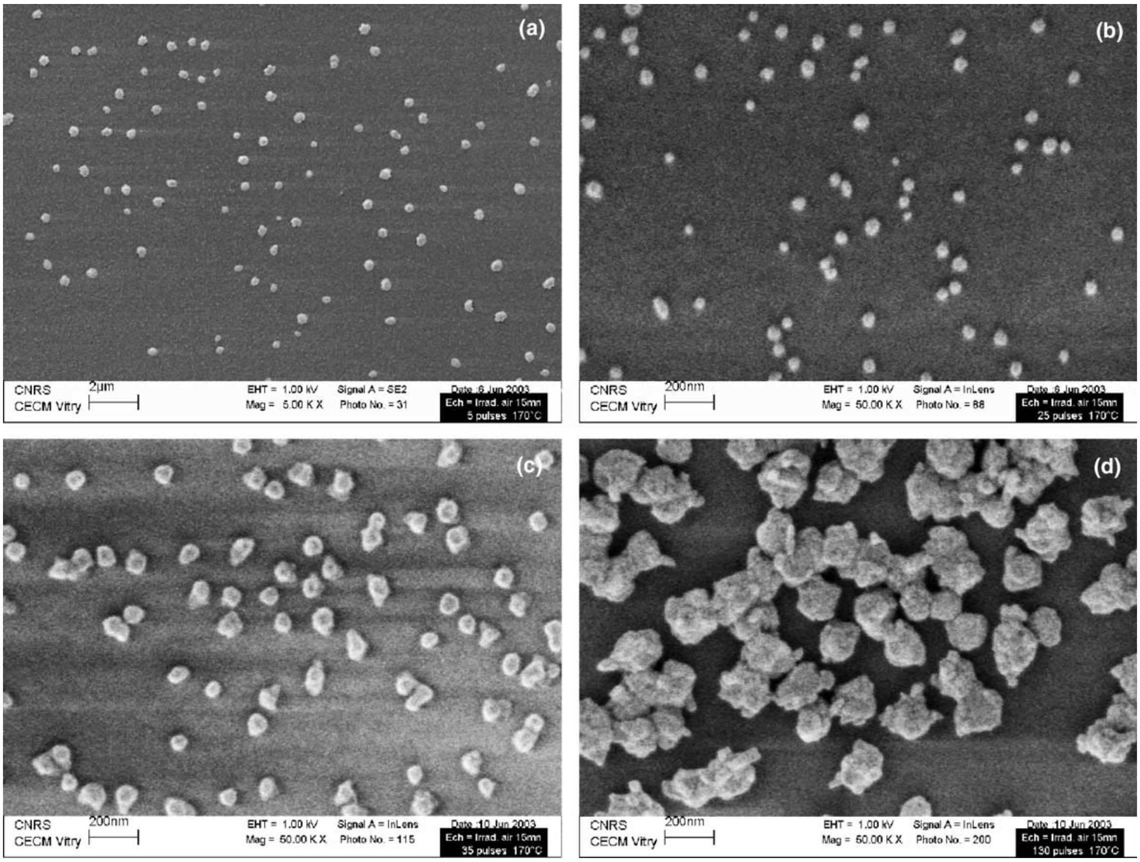

Fig. 2. Typical SEM images of the surfaces of MPTMS treated and subsequently UV-light irradiated SiO_2 substrates after Cu CVD performed at substrate temperature of 170 °C with (a) 5, (b) 25, (c) 35 and (d) 130 pulses.

almost spherical accumulations of Cu which for each substrate have almost the same size. These are aggregates of Cu refereed to as clusters or grains. By neglecting at the moment an initial increase at each substrate temperature, of the clusters density for very short injection times (which will be analysed in detail later), it is seen that the clusters are getting larger in size at longer times and a "layer" like deposit does not form onto the gaps among clusters (compare for example to each other the images in Fig. 1(c) and (d) or in 2(c) and (d) or in 3(c) and (d)). These quick observations allow us to draw the first general conclusion about the nucleation behaviour of Cu onto the thiol treated (and subsequently UV-light irradiated) SiO_2 surfaces studied here: the nucleation takes place following the so-called island or Volmer-Weber growth mode [14], where small clusters are nucleated directly onto the surface and then grow into islands of the condensed phase. It is well known by investigations which have been performed at the past in other systems, that this type of nucleation and crystal growth is typical of metals on insulators. Thus it is not surprising to be observed also in the present case of Cu nucleation onto the thiol surface which is an insulator as well.

In order to be able to follow easier and understand the change of the clusters density with precursor injection time, SEM images were taken on at least five different places on each substrate surface and the number of clusters were counted visually on the images and averaged. In the graph of Fig. 5(a), the resulting clusters densities are plotted versus precursor injection time for

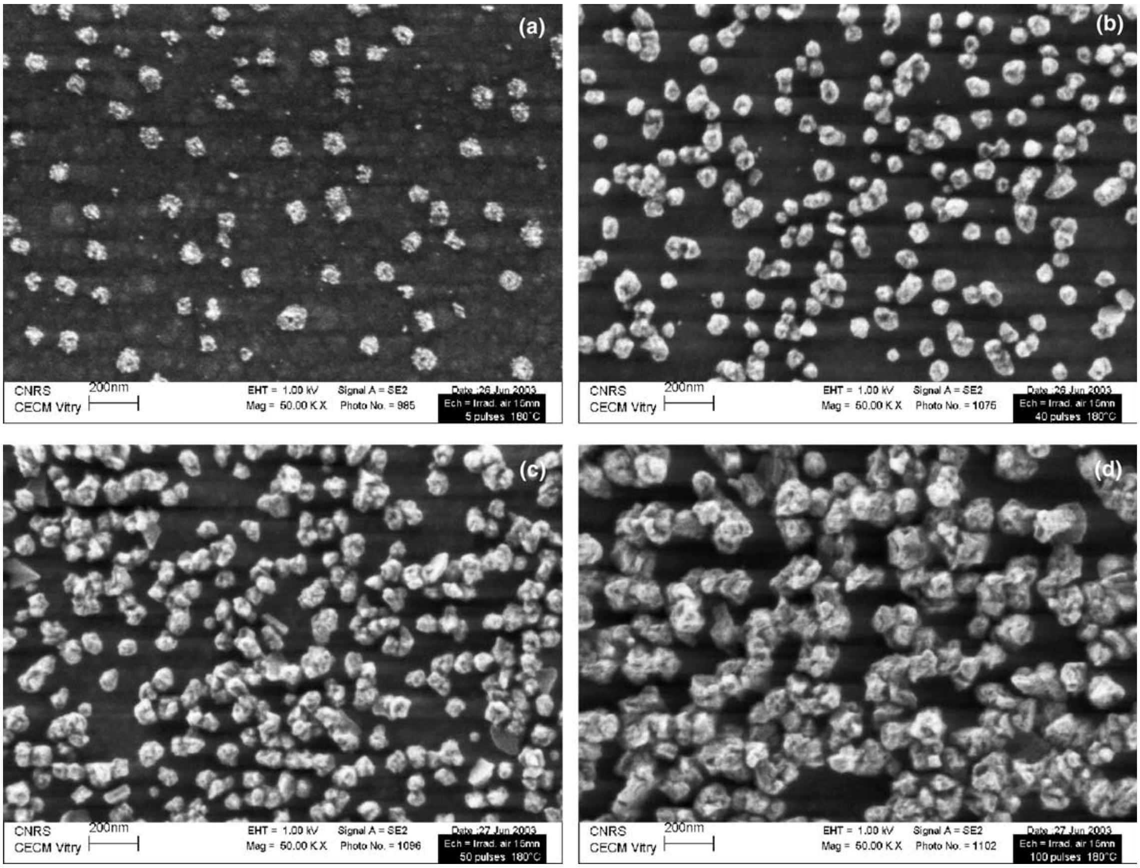

Fig. 3. Typical SEM images of the surfaces of MPTMS treated and subsequently UV-light irradiated SiO_2 substrates after Cu CVD performed at substrate temperature of 180 °C with (a) 5, (b) 40, (c) 50 and (d) 100 pulses.

substrates corresponding to the ones shown in Figs. 1–4.

Considering now in more detail the change of Cu clusters density with precursor injection time for substrates held at the lowest temperature of 160 °C (circle points in Fig. 5(a)), it is seen that the density initially increases with time until it reaches a maximum of around 6×10^{9} cm^{-2} at 15 ms. This is due to the increase of the number of clusters per unit area, as it is also seen when comparing for example the image in Fig. 1(a) with the one in 1(b). The size of the clusters also increases by a negligible amount, but the rate of increase of the number of clusters per unit area dominates over the rate of increase of their sizes. Note that no clusters were formed on the substrate surface at this temperature for 2, 5 and 10 pulses. The observed increase of clusters density with a negligible increase of their sizes, indicates that at the very initial stages of nucleation the precursor molecules nucleate mostly onto the gaps among the clusters rather than onto the already formed clusters. On the other hand for each substrate the nuclei have almost the same average size and this indicates a kind of ‘‘uniform’’ nucleation of precursor molecules at these low substrate temperatures. After the clusters density reaches a maximum, it starts decreasing for longer injection times and at the longest measured time of 90 ms, the density has decreased by almost one order of magnitude to the value of around 5×10^{8} cm^{-2} (Fig. 5(a)). This decrease of clusters density for longer times, after attaining the maximum, is now due to an increase of the size of clusters, as it is clearly seen when

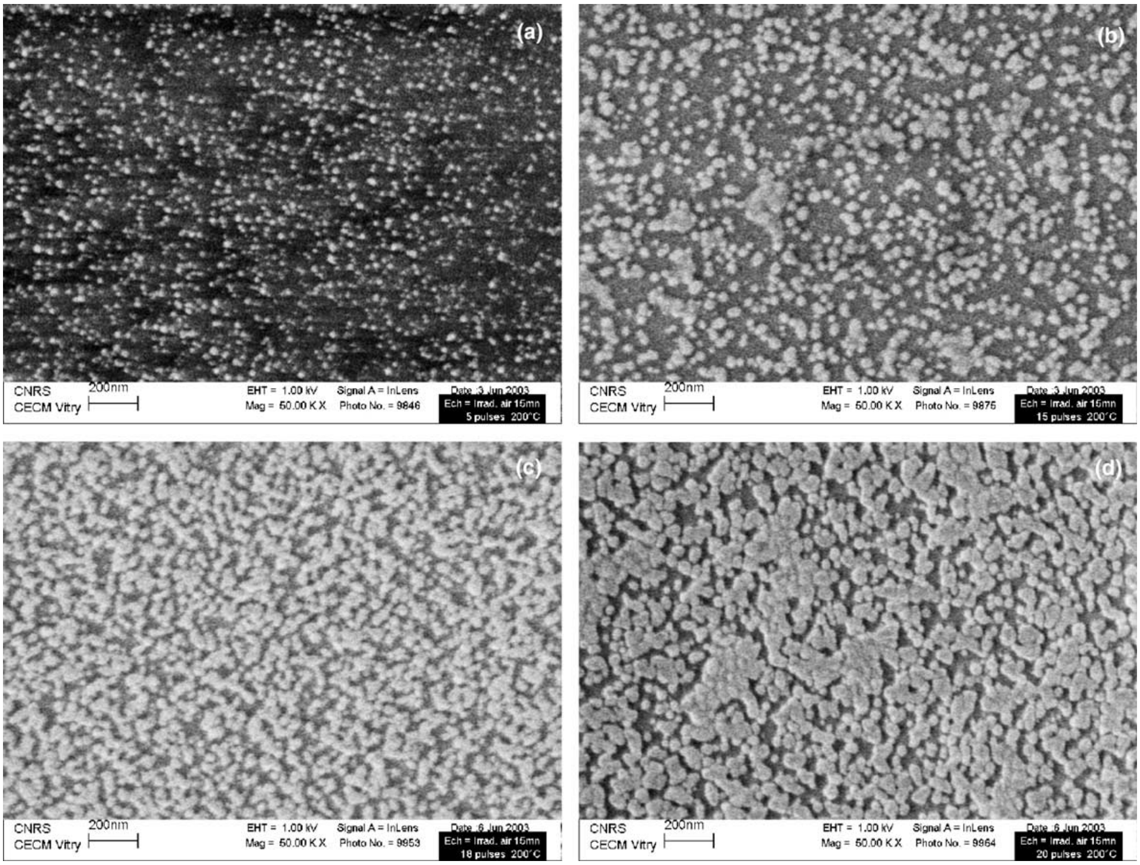

Fig. 4. Typical SEM images of the surfaces of MPTMS treated and subsequently UV-light irradiated SiO_2 substrates after Cu CVD performed at substrate temperature of 200 °C with (a) 5, (b) 15, (c) 18 and (d) 20 pulses.

comparing for example the image in Fig. 1(c) with the one in 1(d). For example the clusters average area is around 5200 nm^2 at 26.25 ms (Fig. 1(c)) while at 45 ms this area has increased to 11,400 nm^2 (Fig. 1(d)). This results in a decrease of the total number of clusters per unit area.

The same Cu nucleation behaviour at the initial stages of nucleation is observed at higher temperatures of 170 °C (images in Fig. 2(a)–(d)) and 180 °C (images in Fig. 3(a)–(d)). The clusters density initially increases up to 15 ms (square points for 170 °C and triangle points for 180 °C, in the graph of Fig. 5(a)) due to an increase of the number of clusters per unit area with a negligible increase of their sizes (compare for example to each other the images in Fig. 2(a) and (b) or in 3(a) and (b)), while after reaching the maximum value, the clusters density decreases for longer times due to an increase of the clusters size (compare for example to each other the images in Fig. 2(c) and (d) or in 3(c) and (d)). Eventually at the later stages of nucleation, coalescence is obtained (images in Figs. 2(d), 3(c) and 3(d)). It is clearly seen, as it has already been pointed out previously, that all clusters for the same image (in Figs. 2(c), 2(d), 3(b) and 3(c)) have almost the same size. This indicates a somehow "uniform" increase—by the same amount—of the size of each cluster, with the number of pulses. Therefore it is concluded that this coalescence (in this region of substrate temperatures below 180 °C) is not obtained by the formation of a "residual" deposit onto the gaps among clusters, but rather by an increase of the size of already formed clusters. When the clusters

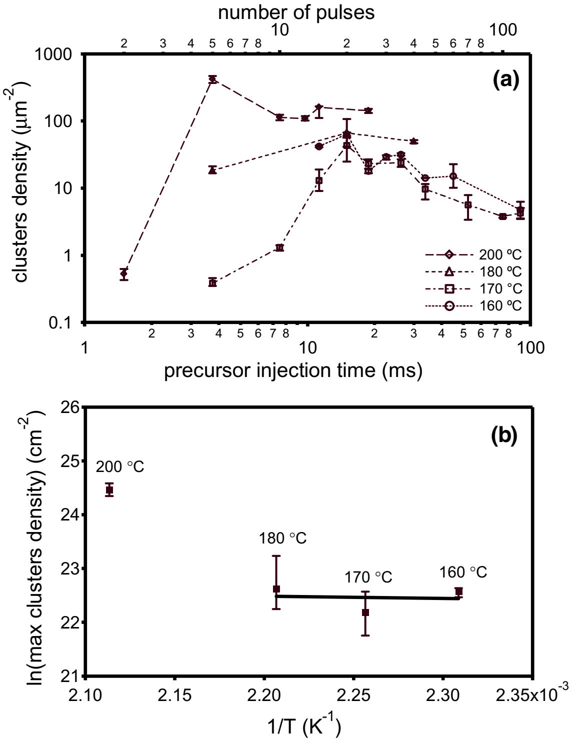

Fig. 5. (a) Clusters density versus precursor injection time (bottom scale) or number of pulses (top scale), for each substrate temperature, extracted from the images in Figs. 1–4. (b) Maximum clusters density in logarithmic scale versus inverse substrate temperature determined from the graphs in (a).

size has increased enough, the clusters start touching each other leading to coalescence. This is also seen in the images of Figs. 2(d) and 3(c), where the discrete nature of the grains can still be distinguished, although the grains are touching each other. Deep trenches, uncovered by deposit are left among grains.

A discretely different nucleation behaviour of Cu precursor molecules is observed onto substrates heated at a higher temperature of 200 °C (images in Fig. 4(a)–(d)). It is now seen that starting from the very early stages of nucleation (image (a)), the clusters which are formed on the surface have a variety of different sizes. This can be seen better in the image of Fig. 4(b). This indicates that secondary nucleation takes place onto the gaps among nuclei. The average nuclei area (around 500 nm^2) is much smaller than the average area of the nuclei obtained onto substrates heated at lower temperatures, for the same number of pulses. The nuclei density increases to the maximum value, rapidly, within a short time period of 3.75 ms (diamond points in Fig. 5(a)). Note that the diamond points in the graph of Fig. 5(a) correspond to the total nuclei density, i.e. counting both small and large nuclei. Contrary to the behaviour observed at lower temperatures, as the precursor injection time increases, the size of the already formed nuclei increases by a negligible amount and coalescence is obtained by the formation of “new” nuclei onto the gaps among the already existing nuclei. In other words coalescence is obtained by a “filling in” of the gaps among existing nuclei, by newly formed nuclei. This kind of nucleation behaviour can be seen in the series of the images presented in Fig. 4(a)–(d). Discrete grains are hardly distinguished in the large accumulations of deposit due to the very small grains size. This kind of coalescence resembles liquid like coalescence.

The observed nucleation behaviour of Gigacopper molecules on the SAMs of MPTMS on SiO$_2$ substrates which was analysed above, at the initial stages of nucleation (before coalescence), can be explained and understood physically, by considering the two temperature regimes of the CVD process and the mechanisms which control the deposition in each regime [8,11,15]. Deposition rate and thin film properties such as surface morphology, resistivity and step coverage on a variety of substrates in the two regimes of CVD have already been well studied in the literature but only on thick films (well after coalescence). In the low temperatures region defined as the substrate temperatures region below 190 °C, the CVD process is within the so-called kinetically controlled regime where the deposition rate is controlled by the reaction kinetics of precursor molecules onto the substrate surface. Because the substrate temperature is low the precursor molecules which arrive onto the surface does not decompose instantly at the point of arrival, but there is a finite time during which the molecules travel on the surface (by diffusion) before decomposition. At the beginning of nucleation (before the nuclei density reaches the maximum value) the separations (gaps) among originally formed clusters might be much larger than the diffusion length of molecules (due to the still very low surface nuclei density), thus the molecules even after diffusion they decompose before they find an already formed cluster. This results in nucleation and new nuclei formation onto the gaps among grains, resulting in an increase of the nuclei density with a negligible increase of their sizes. However when the nuclei density becomes high enough so as the distances among them to become smaller than the diffusion length of molecules, the new molecules have enough time during diffusion to find an already formed cluster, decompose and nucleate on it. A Cu cluster has the maximum affinity for Cu nucleation as compared to the uncovered by Cu substrate. This results in an increase of the size of stable clusters also with the same rate of increase for all clusters. The total nuclei density becomes lower with time and coalescence is obtained by large grains which are grown in size and eventually start touching each other. The surface diffusion length decreases by increasing substrate temperature.

At substrate temperature of 200 °C, the CVD process is within the beginning of the so-called mass transferred controlled regime, where the deposition rate is controlled only either by the rate of arrival of precursor molecules onto the substrate surface or by the time of diffusion of molecules through the diffusion layer. The substrate temperature is so high that every new molecule which arrives onto the surface decomposes instantly at the point of arrival without any surface migration. This results in the observed secondary nucleation, i.e. formation of new nuclei onto the gaps among already formed nuclei. The nuclei are very small, have a variety of different sizes and each nuclei grows negligibly in size with precursor injection time. Coalescence is obtained by new nuclei which fill the gaps among already formed nuclei.

The Cu nucleation behaviour on the organosilane treated SiO_2 surfaces at the initial stages of deposition, which we observe here, is somehow "opposite" to the Cu nucleation behaviour on SiO_2 and TiN substrates which has been studied at the past in the literature, at the later stages of deposition, well after coalescence, when a continuous thick Cu film has already started growing [8,16]. In that case, in the low temperatures regime of CVD, after coalescence, the grains size increases mostly by lateral growth in two dimensions because the molecules diffuse on the *Cu film* surface and nucleate. There are no uncovered by Cu gaps among grains, thus all sites on the surface—which is Cu film—have equal maximum probability for Cu atoms nucleation. This results in a smooth continuous thick film with very shallow, not well resolved trenches among grains. On the other hand in the high temperatures regime of CVD, because of the absence of molecules surface diffusion, the grains size after coalescence increases vertically due to the local nucleation of molecules at the point of arrival onto the substrate. This results in a rough thick film with deep and well resolved trenches among grains.

3.2. Nucleation parameters

Nucleation and thin film growth processes have been extensively studied in the literature and formulated mathematically in detail, but only in the cases of PVD [14,17, and references therein]. This involves only single metal atoms which are adsorbed onto the substrate from the vapour phase and subsequently migrate onto the surface and nucleate. In our case of CVD process the Cu metal atoms are formed by the disproportionation reaction of molecules on the substrate, thus nucleation and growth kinetics depends not only on the surface migration of atoms and molecules but also on the chemical reaction of the molecules dissociation by which the Cu adatoms are created. In a crude approximation we can apply the main conclusions of the nucleation theory to the present case of molecules which diffuse on the surface and create Cu atoms which nucleate.

From the plot of Fig. 5(a) we can determine quantitatively, a few of the parameters which control the nucleation behaviour such as critical nucleus size and nucleation activation energy. The maximum densities of stable clusters (N_S) extracted from the data of Fig. 5(a), versus inverse substrate temperatures ($1/T$) are plotted in Fig. 5(b). In nucleation theories and under 'steady state' conditions where the single atom concentration on the substrate surface does not change with time, i.e. $dn_1/dt = 0$, the N_S versus T is described by the relation [14,17]:

$$N_S = \frac{n_X(Z)}{\eta(Z)} = N_0\left(\frac{R}{N_0 v}\right)^p \exp(\beta E) \tag{1}$$

where $n_X(Z)$ is the density of stable clusters, $\eta(Z)$ is the dimensionless so-called condensation coefficient depending on the surface coverage Z of the surface by growing clusters. N_0 is the total number of surface adsorption sites (cm^{-2}), R is the rate of arrival of atoms onto the substrate surface ($cm^{-2}\,s^{-1}$), v is the effective vibrational frequency of an adatom ($\sim 10^{11}$–10^{13} s^{-1}), $\beta \equiv 1/k_BT$ (k_B Boltzman's constant). In the above equation the parameter p and the apparent activation energy E are in general functions of the critical nucleus size i (defined such that a cluster consisting of j atoms is stable when $j > i$ while the cluster is sub-critical when $j \leqslant i$), of the surface diffusion energy (E_{dif}), of the desorption energy (E_{des}), of the adsorption energy (E_{ads}) and of the binding energy of a cluster with i atoms (E_i) (the free energy difference between i atoms in the adsorbed state and in the cluster). According to Ref. [17], considering for the shake of simplicity ideal classical gas theory, R in ($cm^{-2}\,s^{-1}$) is given by the relation:

$$R = 3.51 \times 10^{22}(MT)^{-1/2}P \tag{2}$$

where M is the molecular weight (g) of the gas at temperature T (K) and pressure P (Torr) and the prefactor 3.51×10^{22} has units of the gas constant ($8.314\ J\,K^{-1}\,mol^{-1}$) per mole. In our present case of CVD and considering Gigacopper molecules instead of single Cu atoms, it is: $T = 100\ °C = 373.15\ K$, $P = 2$ Torr and $M = 364.75$ g (molecular weight of Gigacopper), then: $R = 1.9 \times 10^{20}$ $cm^{-2}\,s^{-1}$. By considering the average area per molecule of a SAM of MPTMS: 21.4 Å^2 [18], then on the $1\times1\ cm^2$ square substrates which we use, it is estimated $N_0 = 4.7 \times 10^{14}\ cm^{-2}$.

As we have explained in detail in the previous section, at temperatures below 190 °C in the kinetically controlled regime of CVD, the new molecules which arrive onto the substrate surface are consumed mostly on increasing the size of already formed stable clusters rather than forming new ones. This indicates that the rate of arrival of "atoms" onto the surface is greater than the rate of loss of "atoms" from the bulk condensate but lower than the rate of re-evaporation from the surface of single "adatoms". In theories of nucleation of metals on amorphous or polycrystalline substrate surfaces this is the main characteristic of nucleation in the so-called "initially incomplete" condensation regime [14,17]. In this regime condensation is incomplete but clusters capture "atoms" by surface diffusion (by the time coalescence starts though, we may well have effectively complete condensation). There is a nucleation barrier for the growth to occur. In this case for 3D islands, it is $p = 2i/5$ and $E = (2/5)(E_i + iE_{ads})$. By fitting a straight line to the three points of Fig. 5(b) (according to Eq. (1)) in the temperature region 160–180 °C and taking into account the values of the several parameters mentioned above, we get $i = 2 \pm 1$ and $E = 0.032 \pm 0.010$ eV.

The variation of nuclei density with precursor injection time and of the maximum density with substrate temperature which we observe here onto the surfaces of irradiated SAMs of MPTMS on SiO_2 substrates, is different to the variation observed on TiN [8,11,19,20], or Ta and TaN substrates [21], but resembles closely the one observed on bare, untreated SiO_2 surfaces where an almost substrate temperature independent maximum nuclei density was also observed [19]. That was taken as a suggestion of Cu nucleation at defect sites. In our case these defect sites may be the $Cu^{(I)}$ atoms which are produced by the reaction of the first precursor molecules with the sulfonic acid headgroups of the irradiated SAM surface, as we have explained in detail in Ref. [7]. Furthermore, the lower value of the activation energy which is determined here (compared to the value of 0.67 ± 0.11 eV for TiN) indicates that the free energy barrier for nucleation and formation of stable clusters is low and this is consistent with the fact that surfaces of irradiated SAMs of MPTMS on SiO_2 substrates have maximum affinity for Cu CVD. Furthermore the relatively small size of critical nucleus indicates that the physical barrier for nucleation is negligible compared to the surface reaction rate. Thus the nucleation rate is controlled mostly by the surface chemical reaction rather than by the formation of clusters of critical size.

3.3. Surface statistical parameters

AFM imaging of the surfaces of substrates (of which SEM images are shown in Figs. 1–4), results in the determination of surface statistical parameters. A few representative AFM images of the substrate surfaces are shown in Fig. 6(a)–(d). CVD was performed with 100 pulses at substrate temperature of 160 °C (a), 170 °C (b) and 180 °C (c), and with 20 pulses at substrate temperature of 200 °C (d). In Fig. 7 the rms surface roughness at different precursor injection times is plotted for two representative substrate temperatures (170 and 200 °C) while in the inset, the rms roughness and average and maximum surface heights versus temperature for the same number of pulses, extracted from the images in Fig. 6(a)–(d), are plotted.

In general for the same substrate temperature, surfaces corresponding to depositions performed with increasing number of pulses at the initial stages of nucleation, before coalescence, are characterized by increasingly higher roughness. At the beginning, depositions with low number of pulses result in the formation of only a few clusters on the substrate surfaces, with small size, thus the rms roughness is low. On surfaces where depositions were performed with higher number of pulses, the clusters density and sizes increase and this results in higher surface roughness.

From the images presented in Fig. 6(a)–(c), it is seen that at substrate temperatures below 190 °C, gaps among grains are still obtained even after depositions performed with the 100 pulses. However at substrate temperature of 200 °C an almost continuous film is obtained, even with only 20

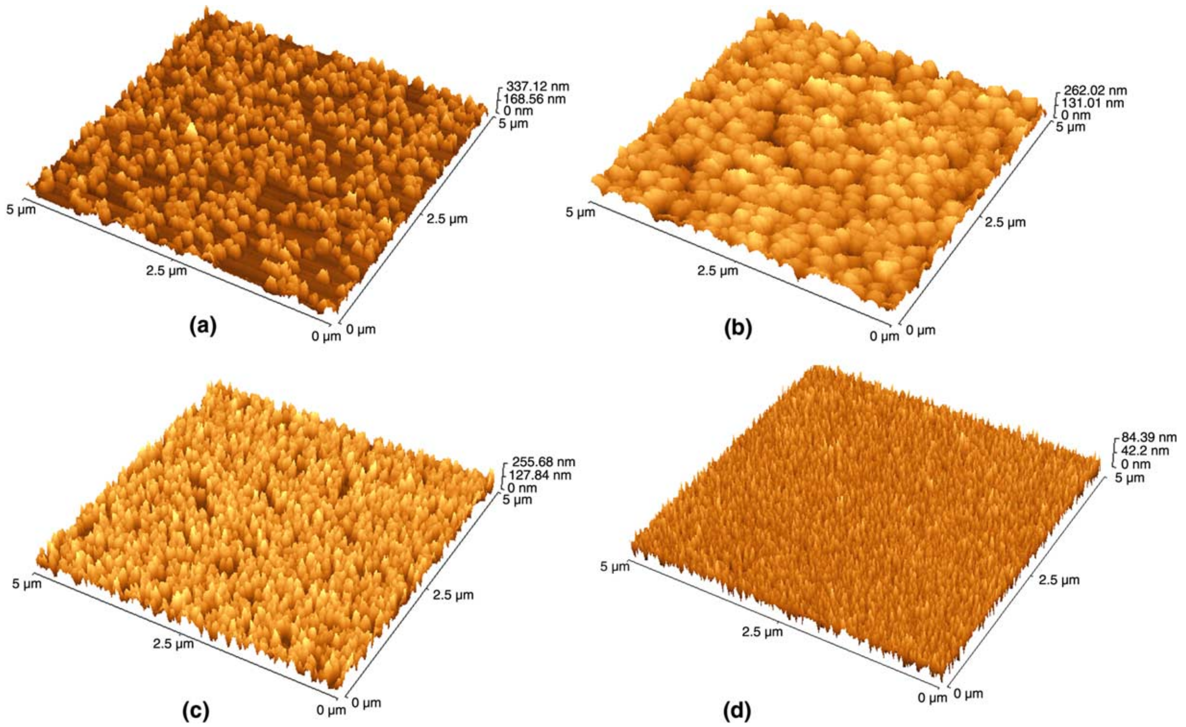

Fig. 6. Typical AFM images of the surfaces of MPTMS treated and subsequently UV-light irradiated SiO_2 substrates after Cu CVD performed with 100 pulses at substrate temperature of 160 °C (a), 170 °C (b), 180 °C (c) and with 20 pulses at 200 °C (d).

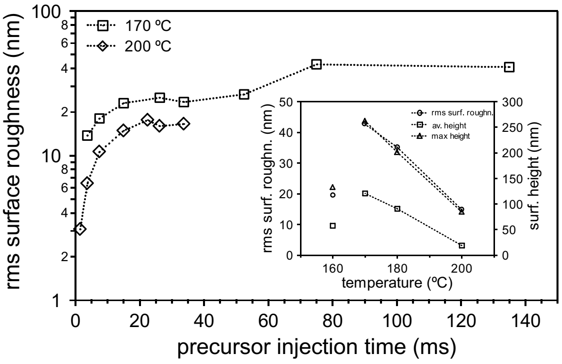

Fig. 7. rms surface roughness versus precursor injection time at different substrate temperatures. Inset shows the roughness and average and maximum surface heights versus substrate temperature extracted from the images in Fig. 6.

pulses deposition. This film has the lowest roughness (which is due to the fact that the clusters which are formed on the substrate surface at this temperature have very small size) and also the lowest surface height as it is seen in the graph presented in the inset of Fig. 7.

4. Conclusions

We have investigated in detail the Cu nucleation behaviour, by CVD, at the initial stages (before coalescence), on irradiated SAMs of MPTMS on SiO_2 substrates. At temperatures below 190 °C nucleation of Cu atoms occurs mostly on already formed clusters due to the diffusion of precursor molecules on the substrate surface before decomposition, while at 200 °C nucleation occurs also onto the uncovered my material gaps among clusters due to the instantaneous decomposition of molecules at the points of arrival onto the substrate. The maximum clusters density is substrate temperature independent below 190 °C. This indicates nucleation at surface defect sites. Lower apparent activation energy for nucleation as compared to TiN, indicates that it is easier to obtain Cu nucleation on the surfaces of irradiated SAMs of MPTMS on SiO_2 substrates rather than on TiN surfaces consistent with the fact that these surfaces exhibit maximum affinity for Cu CVD.

The importance of our data lies to the fact that on the surfaces of SiO_2 treated with MPTMS and subsequently UV-light irradiated, "liquid like" coalescence which will lead to the growth of a continuous film, is obtained with a very low amount of vapour precursor at high temperatures i.e. 200 °C which lies at the beginning of the mass controlled regime, instead of lower temperatures at the end of the kinetically controlled regime. Films grown under these conditions are characterized by low surface roughness and low average surface height. This indicates another superior property of the MPTMS SAMs as barriers for Cu diffusion into Si/SiO_2 structures, that a thinner conformal film could be obtained.

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