

Importance of Implantation Sequence in the Formation of Nanometer Size Colloid Particles Embedded in Amorphous SiO₂: Formation of Composite Colloids with Cu Core and a Cu₂O Shell by Coimplantation of Cu and F

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A striking difference in the properties of nanosized colloid particles between amorphous SiO₂ substrates implanted with Cu and F ions in a differing sequence is reported. No significant change in an optical band peaking at 2.2 eV due to plasma oscillation of Cu nanosize colloids is observed by implanting F and then Cu. The 2.2 eV band is not perceived with implantation of F ions into Cu-implanted substrates. Although colloid particles identified are Cu in the former sequence, those formed in the latter have a dual structure composed of Cu (core) and Cu₂O (shell). This is explained by oxidation of the outer part of Cu colloids by energetic O recoiled from the silica structure by implanted F.

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In recent years, nanometer sized metals and semiconductors embedded in dielectrics such as glass have attracted much attention because of the fundamental interest in zero-dimensional features of the electronic state and potential application as photonic switching based on a large third order optical susceptibility [1]. Fabrication of these composites by means of ion implantation have now been demonstrated [2–9], and a criterion to predict the colloid formation in SiO₂ glasses has been proposed [10]. A variety of nanosized colloid particles, including materials chemically active in ambient atmosphere such as amorphous phosphorus [11], can be fabricated by ion implantation without subsequent thermal annealing. Coimplantation, sequential implantation of various kinds of ions, is a very important technique for producing nanosized colloids of compound materials. In coimplantation, the primary variable parameter to be considered is the sequence of implantation. Although reports have been made on coimplantation [12–14], no conspicuous difference in results between differing implantation sequences has been reported so far, to my knowledge. Here, I report a striking difference in results from different implantation sequences, the optical absorption spectra and structure of nanosized colloid particles formed by changing the implantation sequence of Cu and F ions. The difference is explained in terms of a model combining energy depositions with chemical interactions of implanted F ions with ions in amorphous SiO₂ [15].

Substrates used are synthetic SiO₂ glass plates 20 mm × 20 mm × 1 mm thick. Copper and fluorine ions were implanted at room temperature at an energy of 160 keV to a nominal dose of 6×10^{16} cm⁻² and 160 keV or 40 keV to a dose of 1×10^{17} cm⁻², respectively, and a dose rate of respective ion was ~ 2.5 μA/cm². For comparison, Ne ions (in place of F ions) were implanted at 50 keV to a dose of 1×10^{17} cm⁻². Transmission electron microscopic (TEM) observation was made on substrates parallel to implanted layers. Preparation procedures of specimens were described in a previous paper

[4]. An acceleration voltage of 300 keV was applied for observation. Optical absorption spectra were measured with a conventional dual beam spectrophotometer, and a microbeam attachment (beam spot 30 μm diameter) was used for the measurement of selected portions of the specimen. Gases desorbed from implanted substrates upon heating were analyzed with a thermal-gas analyzing instrument [16], which consists of a high-vacuum system, a quadrupole mass spectrometer, and an electric furnace.

Figure 1 shows optical absorption spectra of substrates implanted with Cu and/or F ions. Absorption extending from ~ 5 to ~ 1.5 eV, including a band peaking at 2.2 eV, is seen in the Cu-implanted substrate. This absorption is due to plasma oscillations of nanosized Cu colloid particles [4,7,17–19,20]. A weak absorption band peaking around 5 eV, which is ascribed to oxygen-related point defects [21] in silica substrate structure, is observed in F-implanted substrates. It is noted in Fig. 1(a) that there is a striking difference in Cu colloid absorption between substrates coimplanted with Cu and F (40 keV) in different sequence. No significant change in the intensity of the 2.2 eV band was perceptible between the substrates implanted with F ions followed by Cu and implanted with Cu alone. On the other hand, in the substrate coimplanted in the reverse sequence (Cu → F), the intensity of whole Cu-colloid absorption was greatly reduced to an extent that the sample appeared almost colorless. No such difference was seen between substrates coimplanted with Cu and F, both at 160 keV in different sequence [Fig. 1(b)], or between substrates implanted with Cu and implanted with Cu followed by Ne [Fig. 1(c)].

Figure 2 compares range and range of straggling of implanted ions along with energy depositions of implanted F ions implanted at 40 and 160 keV. These quantities were calculated with the TRIM code [22]. It is evident that the range of F ions implanted at 40 keV is close to that of Cu (160 keV) ions, but the range of F ions at 160 keV is much deeper than that of Cu. There is no overlap in the depth distributions of the ions in the latter.

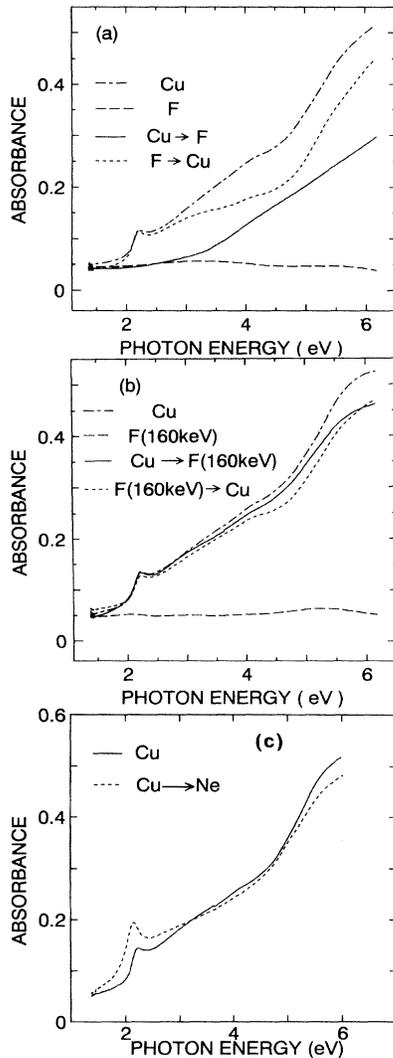


FIG. 1. Optical absorption spectra of implanted $a\text{-SiO}_2$ substrates. Dose: Cu $6 \times 10^{16} \text{ cm}^{-2}$, F $1 \times 10^{17} \text{ cm}^{-2}$, Ne $1 \times 10^{17} \text{ cm}^{-2}$. (a) Acceleration energy: Cu 160 keV, F 40 keV; (b) Cu 160 keV, F 160 keV; (c) Cu 160 keV, Ne 50 keV. Acceleration energies of 40 keV for F ions and of 50 keV for Ne ions were chosen so as to match the peak depth of Cu ions implanted at 160 keV.

Figure 3 shows cross-sectional TEM photographs and selected area electron diffraction (SAED) patterns of substrates implanted with Cu and F ions in different sequences. Although numerous nanosized particles are seen in both substrates, a difference is seen in the SAED patterns and the morphology of colloid particles. The rings on the SAED pattern for the substrate implanted with F ions followed by Cu ions can be indexed as arising from only copper, while the rings for the substrate implanted in the reverse sequence can be indexed as a superposition of Cu and Cu_2O . In the latter (Cu \rightarrow F), particles with non-spherical shape are observed and the particle size increases by a factor of ~ 2 , compared with the F \rightarrow Cu sequence.

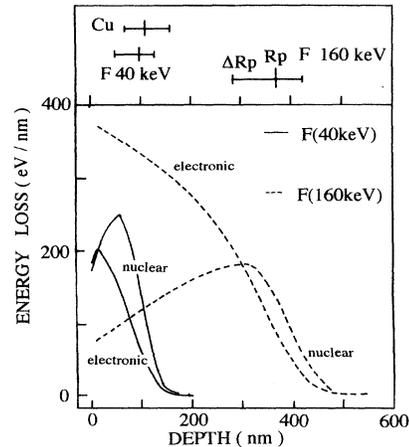


FIG. 2. (Top) range (R_p) and range of straggling (ΔR_p) of implanted Cu (16 keV) and F (40, 160 keV) ions. (Bottom) electronic and nuclear energy losses of F ions implanted at 40 and 160 keV. These quantities were calculated using the TRIM code.

The high resolution TEM photograph in the figure shows the lattice image of the surface of a particle in the substrate (transparent) implanted with Cu followed by F. A few boundaries are seen in the lattice image, showing that the particle is not a single crystal but a secondary particle formed by coalescence of the primary particles. The lattice spacing is 2.47 \AA , which is in agreement with the plane spacing (2.465 \AA) of $\text{Cu}_2\text{O}(111)$.

Figure 4 shows thermal-gas-release spectra of substrates implanted with F ions alone and Cu ions followed by F ions. As reported in a previous paper [23], O_2 gas molecules, which are oxygen interstitials in SiO_2 , are the major defects produced by implantation of F ions into silica. Although desorption of O_2 molecules was observed for both substrates, there is a distinct difference in shape of the desorption spectra between substrates implanted with F alone and with Cu followed by F. Desorption occurs in a single stage centered around 250°C in the substrate implanted with F ions (the concentration of desorbed O_2 molecules up to 650°C is $\sim 3 \times 10^{15} \text{ cm}^{-2}$), whereas the desorption proceeds in the two stages for the substrate implanted with Cu followed by F: The first stage occurs around 250°C , which is almost the same as the temperature corresponding to the peak in the F-implanted substrate, and the subsequent stage starts from ~ 350 and continues to $>700^\circ\text{C}$. The amount of O_2 molecules desorbed up to 300°C ; the temperature at which the first desorption peak ends, and the total O_2 molecules desorbed up to 650°C in the substrate implanted with Cu ions followed by F ions are $\sim 40\%$ and $\sim 80\%$, respectively, of those of the substrate implanted with F ions alone. When the substrate discolored by F implantation (Cu \rightarrow F) was heated once to $\sim 650^\circ\text{C}$, some portions of the substrate turned from colorless to copperlike in color, visually. The inset shows changes in the optical absorption spectrum of the colored portion upon heating. It is evident from the figure that

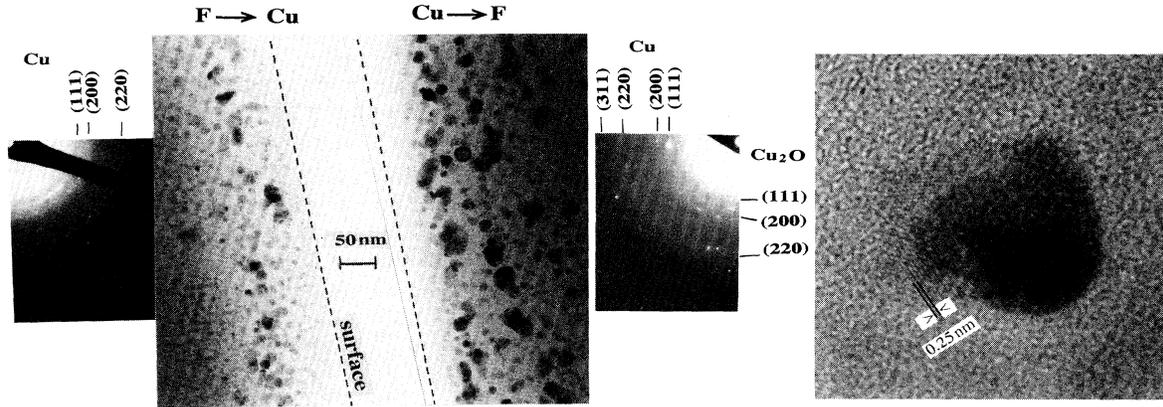


FIG. 3. (Left) cross-sectional TEM photograph of *a*-SiO₂ coimplanted with Cu and F in different sequence. F → Cu: F (40 keV, 1 × 10¹⁷ cm⁻²) followed by Cu (160 keV, 6 × 10¹⁶ cm⁻²); Cu → F: Cu (160 keV, 6 × 10¹⁶ cm⁻²) followed by F (40 keV, 1 × 10¹⁷ cm⁻²). Also shown are selected area electron diffraction patterns indexed to Cu and Cu₂O. (Right) high resolutional TEM photograph of colloid particles formed in sequence of Cu → F, showing a lattice image of spacing of 0.25 nm corresponding to Cu₂O (111) spacings.

the absorption band peaking at 2.2 eV is restored. The intensity of this band relative to that in the Cu-implanted substrate was ~80%. No such a change was observed for the substrate heated to temperatures <300 °C.

We now discuss the cause of the differences due to the implantation sequence. Comparison of the range (see Fig. 2) of Cu with F ions implanted at 40 or 160 keV shows that disappearance of absorption band due to Cu colloid particles is seen only for the case that the range of Cu and F ions is well overlapped. In energy deposition shown in Fig. 2 (bottom), elastic nuclear collision loss is prominent for a combination of 160 keV Cu and 40 keV F ions. On the other hand, for a combination of 160 keV Cu and 160 keV F, electronic energy deposition is predominant, because implanted F ions pass through the range of Cu. Therefore, I conclude that an elastic nuclear collision process plays a role in the disappearance of the Cu plasmon band. It is a plausible model that Cu colloid particles are destroyed by collision with implanted F ions [24]. It is, however, obvious from Fig. 1(c) that this model cannot explain the present results. Despite that the atomic number (*Z* = 10) of Ne is larger than that (*Z* = 9) of F, i.e., nuclear energy deposition *N_e* > *N_F*, the 2.2 eV band is distinctly seen in the substrate coimplanted with Cu followed by Ne [25]. This result strongly suggests that *chemical interactions* of implanted F with ions in substrates dominate key events. Chemical interaction of implanted ions with amorphous SiO₂ substrates is specific to the type of implants [23]. We revealed in a preceding paper [23] that implants (A) with electronegative nature, such as F ions, replace oxygen atoms in the substrate structure and form Si-A bonds, producing O₂ molecules at concentrations comparable to those of implanted F. Combined results of energy deposition and chemical interaction lead to the recombination of oxygen atoms displacively recoiled by implanted F ions [26] to react to each other to form O₂

molecules. On the basis of these considerations, the coimplantation effects observed here are explained as follows. When F ions are implanted in Cu-implanted substrates, elastic nuclear collision energy deposited to substrate structures induces two events. One is the coalescence of Cu colloid particles, as reported in the previous paper [4]. The other is the oxidation of the Cu colloid particles, i.e., recoiled oxygens, which were generated in the displacive reaction of implanted F ions with Si-O bonds in the lattice, have high kinetic energy, and react with Cu colloid particles to form dual structured colloid particles composed of Cu₂O (shell) and Cu (core). In the case of the reverse sequence (F → Cu), Cu colloids are predominantly

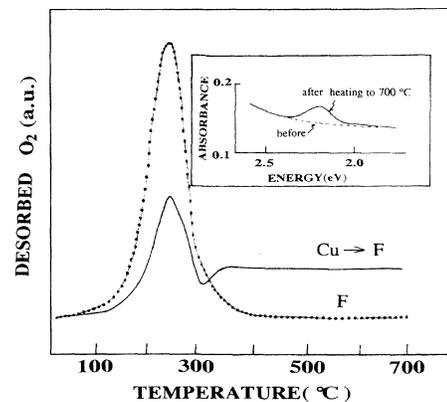


FIG. 4. Thermal desorption spectra of O₂ molecules from implanted substrates. Heating rate: 5 °C/min —, Cu (160 keV, 6 × 10¹⁶ cm⁻²) → F (40 keV, 1 × 10¹⁷ cm⁻²); ·····, F (40 keV, 1 × 10¹⁷ cm⁻²). The concentrations of desorbed O₂ molecules up to 650 °C in F-implanted and coimplanted substrates were 3 × 10¹⁵ cm⁻² and 2.4 × 10¹⁵ cm⁻², respectively. Inset shows changes in the optical absorption spectra of the coimplanted (Cu → F) substrate with heating. ---, before heating; —, after heating to 700 °C. Note that thermal restoring of the 2.2 eV band is distinctly observed.

formed instead of Cu_2O colloids, even in silica matrices trapping O_2 molecules: The charge state of incoming Cu is considered to be neutral in $a\text{-SiO}_2$. The diffusion coefficient of a neutral atom (Cu^0) is extremely larger than that (Cu^+) of an ion in solids. As a consequence, the formation of Cu colloids occurs in preference to that of Cu_2O colloids. Contrary to the present case, when second implants are stable as a charged state, a chemical reaction between both ions is expected to occur. Such a hypothesis may explain the results reported so far: In the case of $\text{Cl} \rightarrow \text{Cu}$ implanted $a\text{-SiO}_2$ [27], Cu colloid formation occurs predominantly as in Cu-implanted substrates, while in the case of sequential implantation of Si (no Si colloid formation occurs in Si-implanted substrates to influence what we discuss here) and N [13], Si-N bonds are formed and no distinct difference between both sequences is noted. Cu_2O is thermodynamically unstable at high temperatures, dissociating into Cu and O_2 [28]. Restoration of the 2.2 eV band upon heating is consistent with the formation of composite nanoparticles with a Cu core and Cu_2O shell.

Optical absorption spectra of colloidal copper particles in dielectrics can be well fitted by the Maxell-Garnett theory, which incorporates size corrections to the imaginary part of the dielectric function [17–19]. According to the calculation, intensities of the absorption due to Cu colloid particles sharply decrease when the particle diameter decreases to <5 nm [19]. Although apparent particle size of colloids are increased by implantation of Cu followed by F, I assume that the diameter of the Cu core in the resulting $\text{Cu}_2\text{O}/\text{Cu}$ particles is <5 nm.

Enormous enhancement of third-order nonlinear optical susceptibility and reduction of threshold intensity for intrinsic optical bistability were predicted for nanosized composite colloid particles by model calculations [29,30]. Since then, interest in optical properties of composite colloid particles is rapidly emerging. The present Letter reports, to my knowledge for the first time, that nanosized composite colloid particles embedded in a solid have been synthesized. Since fine particles are formed in buried layers by implantation, it is possible to stabilize chemically unstable states in an ambient atmosphere. Hence, coimplantation is a method by which a variety of composite colloids by an appropriate combination of ions, implantation sequence, and substrate materials can be synthesized.

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 [25] The intensity of the Cu plasmon band increased after subsequent Ne-implantation in Fig. 1(c). Since intensities of the plasmon band increase with Cu colloid size (Refs. [17–19]), the colloid size is considered to increase after subsequent implantation. This idea is consistent with the observation reported in Ref. [4(b)].
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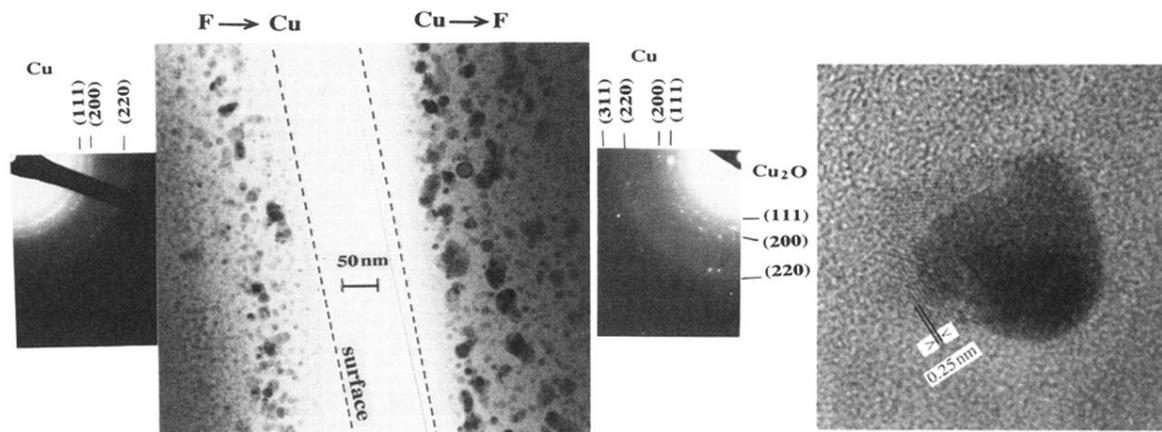


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