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Surface modification of sapphire by ion implantation

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ABSTRACT

The range of microstructures and properties of sapphire (single crystalline Al_2O_3) that are produced by ion implantation are discussed with respect to the implantation parameters of ion species, fluence, irradiation temperature and the orientation of the ion beam relative to crystallographic axes. The microstructure of implanted sapphire may be crystalline with varying concentrations of defects or it may be "amorphous", perhaps with short-range order. At moderate to high fluences, implanted metallic ions often coalesce into "pure" metallic colloids and gas ions form bubbles. Many of the implanted microstructural features have been identified from studies using transmission electron microscopy (TEM), optical spectroscopy, Mössbauer spectroscopy, and Rutherford backscattering-channeling. The chemical, mechanical, and physical properties reflect the microstructures.

Keywords: ion implantation, sapphire, optical properties, defect structures, microstructure, metallic colloids

1. INTRODUCTION

The process of ion implantation is nonequilibrium in nature and introduces ion species and defects into a solid without regard to thermodynamic or thermochemical factors; however, the response of the target does reflect its chemical and structural nature. The microstructure that remains after the cascade cool-down period and subsequent changes in microstructure with time or temperature are driven towards the equilibrium conditions.

Interactions of the ion beam with ceramics are more complex than for metals or elemental semiconductors. Ceramics are compounds with two or more chemical species that are distributed over at least two sublattices in an ordered manner. In many instances, atoms displaced during elastic collisions are not likely to come to rest at the lattice sites of the other type. The species have different atomic masses and the energy to displace each from its lattice site may be different. For example, the energy to displace an aluminum ion in sapphire has been reported to be 18 to 32 eV and to displace an oxygen ion, 41 to 76 eV¹.

The above factors determine the manner in which the energy that is dissipated by elastic collisions is partitioned among the target atoms (ions) and, thus, the production of defects. The type of chemical bonding determines the types of defects that exist after the cascade cool-down period. In many insulators, the introduction of a defect or an impurity ion must occur in a manner that maintains overall electrical neutrality; consequently, the point defects may carry an effective charge or impurity-point defect complexes may be introduced.

Although there have been indications for many years that the ionizing component of the irradiation spectrum affects the residual stress and the volumetric changes in irradiated oxides, such effects have been generally ignored. It was argued that the high values of E_d make it unlikely that defects will be produced in most ceramics by ionizing or excitation processes at the energies commonly used in ion implantation. In 1964, Walker noted that electron-irradiation reduced the swelling that had been produced by neutron irradiation of BeO ². Kreft et al. noted features of ion-irradiated Al_2O_3 , MgO and SiO_2 that seemed to be caused by the ionizing component: the level of damage saturated when the ionizing component of the bombarding ion beams was high but not when it was low; residual stresses in ion-implanted samples were reduced when the samples were subsequently irradiated with protons; and, light ions produced less volume swelling (damage) per dpa (displacements per atom) than heavy ions³⁻⁶. Zinkle⁷⁻¹⁰ has noted that the ionizing component has significant effects on the microstructures of Al_2O_3 , MgO , and MgAl_2O_4 (spinel) due to radiation-induced diffusion processes and ionization-enhanced point defect recombination. In these studies, a high ionizing component suppressed dislocation loop formation and enhanced loop growth. Microstructures often exhibited defect denuded zones adjacent to grain boundaries and free surfaces.

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2. IMPLANTATION OF SAPPHIRE (SINGLE CRYSTAL Al_2O_3)

2.1 Structure of Sapphire

Sapphire belongs to the space group $R\bar{3}C$ (rhombohedral). The O^{2-} anions are arranged in an approximately hexagonal close-packed array with the Al^{3+} cations occupying 2/3 of the available octahedral sites in an ordered arrangement. The structure has trigonal symmetry in the basal plane and the a -axes are fixed by the ordered vacant Al-sites. The structure has often been described on the basis of the close-packing of oxygen ions although there are significant deviations from the ideal hcp structure which are related to the electrostatic interactions between the ions. The aluminum ions and holes are arranged to give maximum separation of like charges and a minimum separation of unlike charges, consistent with the bonding between aluminum and oxygen and the maintenance of overall electrical neutrality. According to the Pauling Electronegativity criterion, the chemical bonding of sapphire is 63% ionic in nature.

Although many oxides exhibit deviations from stoichiometry (some as much as several percent), any departure from stoichiometry in sapphire is so small that it cannot be detected by current analytical procedures. Consequently, while it is possible to substitute 3+ impurities for Al^{3+} , impurities cannot be added without creating charge-compensating defects. The vacant octahedral sites are "structural vacancies" and are ordered to maintain the electrostatic forces in the crystal. The free energy of formation for sapphire is among the most negative of any oxide (other than a few rare earth oxides); thus, in any reaction involving displaced or implanted ions with oxygen, the formation of Al_2O_3 will be favored.

2.2 Effects of implantation parameters on the structure of implanted sapphire

The structure of ion implanted sapphire depends upon the implantation parameters or ion fluence, ion species, substrate temperature and the orientation of the ion beam relative to the crystallographic axes. Ion energy in the range of 50 keV to 1-2 MeV appears to have little effect on the displacement damage except to determine the depth distribution of the irradiation-produced defects and the implanted species.

Many studies have found that room temperature implantation of many ions (e. g., Al, Ti, Cr, Mn, Fe, Ni, Cu, Ga, Nb, Mo) produces extensive damage in the near-surface region. This region remains crystalline unless very high fluences or very high values of deposited damage energy density are used. For a review of the studies conducted prior to 1989 see reference 11. Damage (disorder) is often determined from Rutherford backscattering-channeling measurements and represented as χ for the Al-sublattice determined at the position of peak damage. The quantity χ is defined as the ratio of backscattered yield from an aligned (channeling) specimen to that from a randomly oriented specimen. Damage accumulates rapidly at low fluences but typically remains relatively constant for values of peak deposited damage energy (DE) in the range of about 1 to 9 keV/atom. This behavior is illustrated in Fig. 1 for implantation of Cr, Fe, Nb and Ti into sapphire with the ion beam oriented about 7° from the c -axis. The data were normalized in terms of deposited damage energy as calculated using the code E-DEP-1 (P5.0) ¹². These data suggest that dynamic recovery accompanies the production of defects and that the rate of recovery is similar to that of defect production once some background level of defects is reached.

The amount of residual lattice damage again increases at higher values of DE. For example, Bull ¹³ found an amorphous surface ($\chi = 1$) for sapphire crystals having the $\{10\bar{1}2\}$ face implanted with 6×10^{17} Cr/cm². These conditions correspond to a peak damage energy deposition ≈ 50 keV/atom and a chromium concentration equal to half the Al concentration. Ren et al. ¹⁴ reported that (0001) surfaces implanted with 160 keV Fe became amorphous at a fluence between 1×10^{17} and 2×10^{17} Fe/cm², i.e., DE between 10.7 and 21.4 keV/atom.

Amorphization can also occur during room temperature implantation with low to moderate fluences of a few chemical species where it appears to be due to unidentified "chemical" effects. For example, implanting ⁹⁰Zr and ⁹³Nb to the same fluence at similar energy deposition densities give different amounts of disorder ^{11,15}. Since these elements differ by only three atomic mass units, the details of the cascades should be similar; hence, the differences in the disorder appears to originate in some chemical effect during the cool-down period or to an inhibition of defect recovery. Figure 2 contains the RBS spectra for samples implanted with Zr (6.98 keV/atom) and Nb (6.9 keV/atom). The Zr-implantation produced an amorphous layer extending to about 110 nm below the surface. (The surface of the Zr-implanted sample was amorphous at a

Fig. 1. Peak damage in the Al-sublattice as a function of damage energy

Fig. 2. Backscattering spectra from Al_2O_3 implanted with (a) $4 \times 10^{16} {}^{90}\text{Zr}$ ions/ cm^2 (175 keV) and (b) $4 \times 10^{16} {}^{93}\text{Nb}$ ions/ cm^2 (220 keV).

DE level of 3.49 keV/atom.) The RBS spectra for the Nb-implanted crystal indicate only a damaged surface region with χ for the Al-sublattice reaching a maximum value of 0.64.

An analytical electron microscopy study¹⁶ suggested that amorphization may have occurred at a critical concentration. Measurements of the Zr-concentration profile were made in a series of cross-sectioned specimens which had been implanted to

give buried amorphous layers of different widths. The positions of the boundaries of the amorphous region corresponded to a Zr/Al atomic fraction of ~ 0.065 but exhibited no correlation with damage energy deposition profiles, i.e., defect production.

Other ion species that produce amorphous layers at relatively low fluences during room temperature implantation are Sn¹⁷, Zn¹¹, Si¹¹ and C¹¹. The accumulation of damage in the Al-sublattice as a function of deposited damage energy is indicated in Fig. 1 for Zr and Sn.

The RBS-C spectra for Cr implanted into sapphire (150 keV , $4 \times 10^{16} \text{ ions/cm}^2$) at substrate temperatures of 77, 300, and about 640 K, Fig. 3, show that the higher the substrate temperature during implantation, the lower the residual disorder or damage¹⁸. The peak damage in the Al-sublattice is similar for the 300 and 640 K implantations but the disorder in the region from the surface to the peak position is less at the higher temperature. The free surface may be acting as a sink for the irradiation-produced defects.

As indicated by the RBS-C spectra of Fig. 3, implantation at low substrate temperatures ($<100 \text{ K}$) produces an amorphous or random state. The random value of backscattered yield for the Al-sublattice is reached at 0.32 keV/atom for 260 keV Cr-implantation at 77 K (c-axis orientation). Transmission electron microscopy and selected area diffraction patterns confirmed the amorphous nature of the implanted zone, i. e., no coherently diffracting regions greater than 1 nm in size. Figure 4 compares the disorder, χ , in the Al-sublattice as a function of deposited damage energy for Cr implantation at 77 K (liquid nitrogen temperature, LNT) with that at 300 K. That the amorphization is due to damage accumulation and not chemical effects has been confirmed by stoichiometric implants of aluminum plus oxygen at 77 K. Abe et al.¹⁹ detected amorphous regions in thin foils of sapphire irradiated with xenon and krypton ions at temperatures below 200 K. Since almost all the ions passed through the foils, the amorphization was attributed to damage accumulation.

Fig. 3. Rutherford backscattering-ion channeling spectra for sapphire implanted with $4 \times 10^{16} \text{ Cr/cm}^2$ (150 keV) at different substrate temperatures (from reference 30).

Fig. 4. Damage accumulation at 77 and 300 K in Cr-implanted sapphire

The amount of residual disorder is strongly dependent upon the orientation of the ion beam relative to the crystallographic axes, especially at higher fluences^{20,21}. This observation may explain some of the differences in implanted structures reported by different investigators who often have used specimens of different orientations. Figure 5 shows the accumulation of peak lattice disorder at room temperature as a function of fluence for sapphire implanted with 160 keV iron. In each case, the a- or c-axis was oriented about 7° from the beam axis in order to avoid channeling during implantation. The amount of disorder is similar at fluences below 4×10^{16} ions/cm² but the disorder accumulates much faster for the c-axis specimens at higher fluences. For these conditions, the random (amorphous) state is reached at 2×10^{17} Fe/cm² for the c-axis specimen but this condition had not been reached in the a-axis material at 5×10^{17} Fe/cm².

Studies²⁰ on Cr implantation at 77 K have shown that the random state is reached at a fluence of $2-3 \times 10^{15}$ Cr/cm² for the c-axis specimens but only at a fluence of 2.4×10^{16} Cr/cm² for the a-axis samples, an order of magnitude difference. The RBS-C measurements indicated a difference in the manner in which the disorder accumulated.

Bull¹³ and O'Hern et al.²² observed that the measured residual stresses and the hardness changes were lower at a given fluence for the a-axis orientation.

2.2. Structure of ion implanted sapphire

Rutherford backscattering-ion channeling (RBS-C) measurements suggest that the stoichiometry of sapphire does not change during implantation of at least some ionic species²³⁻²⁶. Channeling yield measurements support the conclusion that the number of residual aluminum and oxygen displaced ions occur in the stoichiometric ratio for implantation of Xe and Pt²³, Pb^{24,25} and Al²⁶.

Transmission electron micrographs and selected area diffraction (SAD) patterns for sapphire implanted with cations at room temperature are characterized by a high density of "black spots" typical of point defect clusters. It is likely that they are stoichiometric, interstitial dislocation loops. Zinkle²⁷ identified dislocation loops on {0001} and $\{10\bar{1}0\}$ habit planes for samples implanted to a peak damage energy of 3.1 keV/atom with simultaneous beams of Al and oxygen at room temperature. The Burgers vector was $b = 1/3 \langle 01\bar{1}1 \rangle$ for many of the dislocations.

Fig. 5. Damage as a function of iron fluence for c-axis and a-axis oriented sapphire

Fig. 6. Luminescence spectra of sapphire implanted with 4×10^{16} Fe/cm² (160 keV) excited by indicated wavelengths.

Defects in the anion sublattice can be detected by optical spectroscopy. Samples implanted with cations at room temperature have a characteristic gray-brown color. Optical density (absorption) spectra¹⁴ are characterized by a strong peak in the vicinity of 200 nm (from about 170 to 230 nm) in specimens implanted with 4 to 10×10^{16} Fe/cm². This region contains the location of both F and F⁺ peaks, an oxygen vacancy containing two trapped electrons and an oxygen vacancy containing one trapped electron, respectively. These defects have peaks in the emission spectra at 406 and 331 nm, respectively. The luminescence curves of Fig. 6 clearly show the presence of both types of anion defects in a sample implanted with 4×10^{16} Fe/cm².

Information about the final disposition of the implanted ions can be determined from RBS-channeling measurements if the disorder is relatively low, e. g., at low fluences or in annealed samples. Canera et al²⁵ used axial and planar scans to determine that lead ions implanted into Al₂O₃ occupied sites along the <0001> rows but displaced 0.05 nm from the oxygen planes.

The Mössbauer effect provides a unique probe for investigating the structural aspects of solids on the atomic scale. Measurements of the hyperfine interactions provide information on symmetry, ordering, and chemical bonding in the immediate environment of the probed nucleus.

A combined RBS, TEM, and Conversion Electron Mössbauer Spectroscopy (CEMS) study²⁸ has determined the residual charge state on iron ions implanted into sapphire at room temperature to fluences of 10^{16} to 10^{17} Fe/cm². The matrix remained crystalline for these conditions. Five quadrupole-split doublets and one single line were detected. The doublets were ascribed to three types of ferrous iron (Fe²⁺) and two forms of the high spin state Fe⁴⁺. The single line was identified as arising from metallic iron clusters (Fe⁰).

The Fe²⁺ components were ascribed to isolated or clusters of a few implanted iron ions associated with one to a few oxygen vacancies. The single line was attributed to small metallic precipitates that behave superparamagnetically at room temperature but show magnetic splitting at 4 K. Precipitate particles having a size of 1 - 3 nm were detected by TEM examination and electron diffraction patterns indicate the precipitate to be α -Fe, Fig. 7a. The CEMS results indicate that they are under high hydrostatic pressure.

The high-spin state, Fe⁴⁺, appears only at higher fluences. This state appears to arise from iron ions located in tetragonally-distorted octahedra which contain oxygen vacancies or nonbridging oxygen ions.

The relative amount of each state depends upon the implantation fluence (concentration of iron and amount of damage). At the lowest fluence studied, all the iron is distributed among the three 2+ states. The Fe⁰ state appears at higher fluences and constitutes almost 40% of the iron at 10^{17} Fe/cm². The Fe⁴⁺ state is present only at high fluences where the disorder is high and there are large numbers of oxygen vacancies.

One of the Fe²⁺ components present in the room temperature Fe-implanted sapphire samples (crystalline) was absent in samples implanted to similar fluences at 77 K but which were amorphous²⁹. This component was ascribed to isolated iron ions or to ions associated with one or two oxygen vacancies. Otherwise, the spectra contained the same components as the room temperature samples, but in different proportions. About 20-22% of the implanted Fe was present as Fe⁰ for the entire range of fluence (10^{16} to 10^{17} ions/cm²).

The CEMS spectra for samples of sapphire amorphized by room temperature implantation of tin show the presence of Sn(II) and Sn(IV)¹⁷. One structural model of amorphous tin oxide consists of distorted octahedra having central Sn(IV) linked by Sn-O bonds with bridging Sn(II) at the apex of a pyramid.

Short-range order in the "amorphous" phases was obtained from the fine structure of the electron energy loss spectra¹⁶. The radial distribution function, which gives the Al-O nearest-neighbor distances, was obtained from an analysis of such spectra

Fig. 7. TEM photograph of sapphire implanted with 1×10^{17} Fe/cm² (160 keV) at room temperature; (a) as-implanted, plan view; (b) annealed 1 h 1373 K in Ar-4% H₂, cross-section.

for samples implanted with Al + O and Fe at 77 K. Short-range order was found in both samples, and the details of the SRO depend upon the implanted species. The Al-O first near-neighbor distance in amorphous stoichiometric-implanted sample was similar to that found in γ -Al₂O₃, whereas, in the amorphous Fe-implanted sample it was that of α -Al₂O₃.

3. NANOMETER SIZE IRON DISPERSIONS IN SAPPHIRE

The study of materials having the dimensions of a few nanometers has become possible in recent years due to the development of techniques to prepare clusters and colloids of metals and semiconductors of this size. Dispersions of nanometer size clusters or colloids in polymers or insulators offer the opportunity to study the boundary of the metallic state, i.e., at what size do the physical properties pass from those of giant molecules to those of the metallic (or semiconducting) state?

Ion implantation of metallic and semiconducting elements into insulators offers a unique opportunity to prepare nanometer size dispersions in crystalline or amorphous matrices. The size, shape and composition of such dispersed particles can often be further altered in a controlled manner by post-implantation annealing in selected atmospheres.

Because of the extremely low solubility of impurities in sapphire, there must be charge compensation for the excess (implanted) cations. This may be accomplished by formation of impurity-point defect complexes at low fluences²⁸ and/or the formation of a metallic phase at higher fluences^{28,31}. Metal-ceramic nanocomposite surface layers which may have unique properties can be prepared in this manner. This section summarizes studies on nanometer-size iron particles in sapphire prepared by ion implantation and post-implantation annealing^{14,28,31-33}.

The CEMS study²⁸ indicated that all implanted iron was in the Fe²⁺ state, probably associated with vacancy clusters, for fluences below 2×10^{16} Fe/cm² (160 keV). Optical absorption and luminescence measurements indicated large concentrations of F- and F⁺-centers (oxygen vacancies with two or one trapped electrons, respectively). Second phase particles were not detected in specimens implanted with 4×10^{16} Fe/cm² or less, although the CEMS measurements indicate 18% of the implanted ions were in the Fe⁰ state. The volume fraction of metallic particles would be about 0.02 and the probability of detection by electron microscopy is low. Second phase particles were clearly visible in micrographs taken of these samples annealed for one hour in a reducing atmosphere (Ar-4% H₂) at 1173 to 1373 K. The second phase particles, ranging in size

from 5 to 25 nm, were iron, according to energy dispersive x-ray spectroscopy (EDS). The largest particles are located near the peak implanted iron concentration and the size decreases as the concentration falls from this peak. Each particle located within 70-90 nm of the surface was associated with an attached void.

The RBS-C spectra for the sample implanted with $1 \times 10^{17} \text{ Fe/cm}^2$ showed that the sapphire remained crystalline but was highly damaged in the peak damage region. The CEMS study indicated that 40-45% of the implanted iron was present in the metallic state for this fluence. After removal of approximately 50 nm from the implanted surface before the specimen was back-thinned, a distribution of small, darkly imaging clusters 1 to 3 nm in size was detected by electron microscopy, Fig. 7a. Measurements by EDS with a 2 to 3 nm diameter electron probe showed the clusters to be iron-rich and the diffuse satellite spots in the selected area diffraction (SAD) pattern were consistent with the clusters being α -Fe. Lattice fringes in HREM confirmed the RBS findings that the matrix remained crystalline at this fluence.

If the 1 nm diameter Fe particles were spherical, each particle would contain about 45 iron atoms, or about 1200 atoms for the 3 nm diameter particles. The iron exhibited superparamagnetic behavior at room temperature but magnetic hyperfine splitting at 4.2 K with a field of 330 kOe.

Cross-section micrographs of samples annealed at 1373 K contained images of elongated iron precipitates which were 40 to 60 nm long and up to 40 nm wide, Fig. 7b. The long dimension was parallel to the surface and centered at the location of the peak iron concentration. Smaller precipitates were found deeper into the specimen and closer to the surface. The size distribution shows one group peaked at 17 nm and extending to 35 to 40 nm and another group ranging from 33 to more than 58 nm with a maximum at 45 nm. The large particles exhibited a tendency toward faceting. The long direction of the particles was parallel to the (0001) plane of sapphire. Elongation could be due to rapid diffusion parallel to these close-packed planes, or could be driven by concentration gradient of the implanted iron, e. g., more rapid growth along the line of highest concentration.

Random and channeled RBS spectra from the Al-sublattice for a specimen implanted with $2 \times 10^{17} \text{ Fe/cm}^2$ coincided to a depth of about 260 nm, indicating an amorphous or microcrystalline surface layer. The coincidence of the aligned and random spectra of iron in also suggests the random distribution of iron ions. Examination by TEM confirmed that the sapphire matrix was amorphous. Low magnification electron micrographs gave the impression of "strings" of iron particles lying parallel to the surface. High resolution electron micrographs (e.g., Fig. 8a) showed these 5-10 nm diameter particles to be crystalline and embedded in an amorphous matrix. Electron diffraction confirmed that they were α -Fe. Lattice fringes and electron diffraction showed that the particles were oriented relative to the substrate; hence, the particles initially precipitated while the matrix was still crystalline. The orientation relationship is: $\{011\} \alpha\text{-Fe} \parallel \{001\}_{\text{sapphire}}$ and $\langle 111 \rangle \alpha\text{-Fe} \parallel \langle 310 \rangle_{\text{sapphire}}$. Lattice fringes in the iron particles indicated alignment with three $\langle 310 \rangle$ directions of sapphire. The close-packed directions of iron and sapphire are not quite parallel, probably due to the misfit strains. The misfit strain is 4.3% along $[1\bar{1}0]$ (or $[1\bar{1}00]$) and 17% along $[110]$ (or $[11\bar{2}0]$) of sapphire.

Electron micrographs of samples implanted with $2 \times 10^{17} \text{ Fe/cm}^2$ and annealed at 1173 K showed a band of iron 25 to 35 nm wide at a depth of 50 nm, Fig. 8b. Many of these platelets extended for several hundred nanometers parallel to the surface. The region between the platelets still contained amorphous material. Some of the light appearing regions may also be cracks introduced by the difference in thermal expansion of the iron and the matrix or a coalescence of vacancies. Elliptical α -Fe particles of 10 to 40 nm in length were also present. The long direction of the platelets was again parallel to the (0001) plane of sapphire. A similar pattern of iron platelets and large particles was observed in samples annealed at 1373 K. Lattice fringes in these micrographs indicated that the amorphous matrix had recrystallized during annealing at 1173 and 1373 K.

4. OPTICAL PROPERTIES OF IMPLANTED SAPPHIRE

The optical properties of sapphire are sensitive to the defect structure produced by ion implantation. These properties are also affected by the distribution and form of the implanted species. Figure 9 illustrates the effects of different implanted species on the infrared transmittance of 1 mm-thick sapphire (c-axis parallel to the light beam)³⁴. The controlled sample had been optically polished and annealed for 5 days in flowing oxygen at 1500° C. The effects of implantation on transmittance increase as the wave length decreases toward the visible spectrum. With the exception of Ga, the decrease in transmittance at 3 μm was 1.5 to 2%. There was little change with ion fluence in the range of $1 - 10 \times 10^{16} \text{ ions/cm}^2$.

Fig. 8. TEM photograph of sapphire implanted with 2×10^{17} Fe/cm² (160 keV) at room temperature; (a) as-implanted; (b) annealed 1 h at 1173K in Ar-4% H₂ (cross-section views).

Fig. 9. Transmittance for annealed and implanted sapphire crystals.

The phase change from crystalline to amorphous caused by ion implantation of sapphire has been used to produce wave guides. The transformation to the amorphous structure is accompanied by a volume expansion of 20 - 25%. This leads to a change in the refractive index of 1.3% which is sufficient for wave guide fabrication³⁵. Using the concept that some ions efficiently trap implantation-produced defects and that the defects have reduced mobility at low temperatures, Townsend et al.

Fig. 10. Optical absorption of sapphire implanted with 1×10^{17} Fe/cm² and annealed in Ar-4% H for 1 h at the indicated temperature.

produced a buried amorphous layer by implanting 6 MeV carbon ions at fluences of 10^{16} to 5×10^{16} ions/cm² at 77 K. Waveguide profiles were analyzed at 488 and 633 nm using dark mode measurements. In all cases dark modes were observed with a depth of the barrier beneath the surface of 2.8 μ m which is very near the position of peak damage production.

Optical absorption spectra for the samples implanted with 1×10^{17} Fe/cm² and those annealed in the reducing atmosphere are contained in Fig. 10. The strong absorption band at about 200 nm is due to F-centers (F- and F⁺). The optical density of this band, which is proportional to the concentration of the F-centers, decreases as the annealing temperature is increased. Annealing produces two additional peaks in the spectra, one at about 265 nm and a broad band in the range of 320 to 360 nm. The F⁺-center has absorption peaks at 229 and 256 nm in addition to the one at 197 nm³⁶; however, the intensity of this peak increases with annealing temperature and the absorption at 197 nm decreases. The TEM photographs show the size of iron precipitates to increase with annealing time and temperature and to exhibit a bimodal distribution of sizes. The absorption in this range is attributed to Mie scattering from the iron particles.

5. SUMMARY

The structure of ion implanted sapphire may be crystalline with point defects, point defect-impurity complexes, and dislocations or it may be amorphous. The structure depends upon the implantation parameters of ion species, ion fluence, substrate temperature and orientation of the ion beam relative to the crystallographic axes. The amorphous state contains short-range order whose details is affected by ion species. In general, the lower the temperature and higher the fluence, the more disorder that is retained. Certain ion species appear to stabilize the disorder against dynamic recovery during implantation and thus promote the amorphization.

Changes in chemical, physical and mechanical properties reflect changes in the structure. In this paper, changes in optical properties were described.

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