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Characteristics of Cu implantation into Si by PBII using UBMS cathode ①

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[Abstract] The implantation of Cu into Si substrate was carried out by plasma-based ion implantation (PBII) using unbalanced magnetron sputtering (UBMS) cathode as the metal plasma source. The different pulse bias (U_p) and the distance between the cathode and the samples (d_{s-t}) were chosen to research the characteristics of this method. The results show that the implantation of metal ions can be realized by the metal plasma source of UBMS cathode. The physical process such as the metal ion pure implantation, the gas ion implantation, the recoil implantation of the metal atoms, the deposition of the metal particles and the re-sputtering of the metal film depend on the energy, dose and deposition rate of the ions (Cu^+ , Ar^+). The metal plasma based ion implantation of Cu into Si substrate is favored by selecting higher U_p(60 kV) and larger d_{s-t}(200 mm).

[Key words] unbalanced magnetron sputtering; plasma-based ion implantation; recoil implantation
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1 INTRODUCTION

The metal plasma based ion implantation (MePBII) is intrinsically different to the conventional gas plasma based ion implantation (GaPBII) due to the condensable feature, larger collision cross section and multivalent ion creation of the metal plasma. There are several kinds of MePBII methods in which different kinds of metal plasma source are used, such as vacuum arc plasma source[1~3], 4π II type ion source[4], ECR sputtering plasma source[5] etc. Compared with other methods used to generate the metal plasma, the magnetic discharge is steady and controllable and the structure of the UBMS cathode is simple. Many studies about UBMS mechanism was carried out[6~8]. The primary work about this method in the authors' group was reported in Ref. [9]. It is a disputable idea that the MePBII is carried out using the unbalanced magnetron sputtering (UBMS) cathode as metal plasma source because of the low ionization rate of UBMS plasma[10, 11]. In this work Si wafers with the lowest sputtering yield are selected to avoid the influence of sputtering of the substrate, and the implantation of Cu into single crystal Si wafers is carried out by PBII using UBMS cathode to investigate the characteristics of this method.

2 EXPERIMENTAL

The experiments were carried out in the industrial prototype DLZ-01 PSII installation. The vacuum chamber was a cuboid chamber with gauge of 700 mm × 700 mm × 1 000 mm and four UBMS cathodes were installed on the wall symmetrically to generate the metal plasma. The further ionization of the metal particles was achieved by the ring antenna installed on the top of the vacuum chamber[12].

The single-crystal Si wafers with N ⟨100⟩ orientation and gauge of 20 mm × 20 mm × 0. 25 mm was fabricated as the substrate. The oxidation layer on the Si wafer was remained to be the label of the original surface. The preliminary samples were cleaned by the ultrasonic cleaner, then placed on the sample holder at distances (d_{s-t}) of 200, 250 and 300 mm from the UBMS cathode, respectively. The vertical distance between the center of the samples and that of the UBMS cathode and the antenna were 60 mm and 600 mm, respectively.

A d130 mm × 5 mm pure copper plate was selected as the target. The UBMS magnet system included a permanent magnet inside and a set of annular electromagnets outside. The degree of unbalanced discharge can be adjusted by changing the coil current density. Ar gas was selected as the work gas; the gas flow rate was 16. 5 mL/s; the outside electromagnetic current was 500 mA; the bias voltage of UBMS cathode was 210 V; the current of the UBMS cathode was 200 mA. The dynamic implantation mode was used, namely the UBMS deposition was carried out in the whole implantation process. The parameters of the ion implantation process were as follows. The pulse high bias were 20 kV, 40 kV and 60 kV, respectively; the based vacuum was 5×10^{-4} Pa; the work vacuum was 0. 1 Pa; the pulse width was 77 μs; the pulse frequency was 100 Hz; the power of radio frequency (RF) source was 500 W; the samples were

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kept at the room temperature.

The depth profiles of copper in Si substrate were measured by XPS (PHI ESCA 5700) with Al K_α (1476.6 eV) radiation. A high vacuum of 10^{-6} Pa was maintained throughout the measurement. The Ar^+ ion beam of 3 keV and 5.86 μA was used for depth profiling. The area of the sputtering scan was 16 mm^2. The sputtering rate of Cu was about 2.37 nm/min and that of Si was about 0.56 nm/min. The analysis and the sputtering were carried out alternately. The thickness of the Cu film was measured by Tencor p-10 instrument. The length of measurement was 200 μm. The scan speed was 20 μm/s. The load was 10 mg.

3 RESULTS AND DISCUSSION

3.1 Recoil energy of Cu and multi-energy ion implantation

PBII is a multi-energy ion implantation process. More ions that possess the implantation energy lower than the largest securable energy are implanted into the substrate[13]. The distribution of implantation ions possessing different energy is related closely to the experimental conditions, such as the kind of ions, pulse bias, RF power and gas pressure etc. Otherwise, because the density of Ar ions is higher than that of Cu ions in metal plasma, the recoil implantation effect (include the collision cascade) made by Ar ions is predominant. The distribution of the recoil energy of Cu atoms delivered by Ar ions with different energies is shown in Fig. 1. It can be found that the maximum recoil energy of Cu atoms is similar when the different energetic Ar ions are used. The depth of Cu atoms in the substrate possessing the maximum recoil energy increases with increasing the incident energy of Ar ions and a long tail of the recoil energy distribution of Cu atoms produced by the collision of the high incident energy of Ar ions. The maximum displacement of the energetic Cu atoms of 160 eV is about 20 nm in Si substrate and 9 nm in Cu. So the recoil implantation effects of the first collision are very small. The collision cascade of the particles (Ar and Cu) plays an important role in the recoil implantation of Cu atoms. Those two effects are called as the recoil implantation.

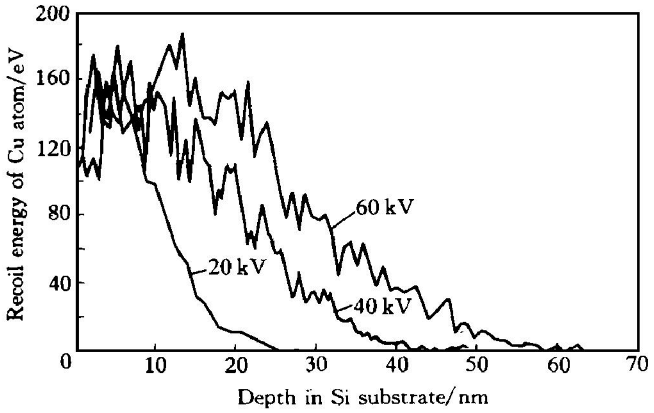

Fig. 1 Recoil energy of Cu atoms in Si substrate by bombardment of Ar^+ with different energies

In order to discuss the pure implantation of Cu ions in the metal plasma, the depth profiles of Cu in Si substrate implanted by Cu ions possessing different energy with the same dose are shown in Fig. 2. It can be found that the depth of Cu in the implantation layer is small but the maximum concentration of Cu is high in the lower energy ion implantation. Because the most ions implanted by MePBII are low energy ions, the content peak of Cu forms at the near surface region.

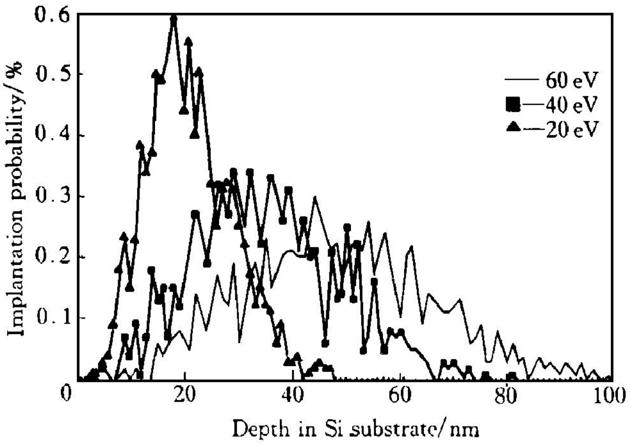

Fig. 2 Profiles of Cu in Si substrate by Cu^+ implantation with different energies

3.2 Deposition rate of Cu at different d_{s-t}

The deposition rate is decided by the amount of metal particles arriving at Si substrate and the dose of metal ions. The deposition rates of Cu particles generated by UBMS with different d_{s-t} are shown in Fig. 3. The deposition rate (about 400 nm/h) at d_{s-t} of 200 mm is 4 times higher than that of 250 mm and 20 times higher than that of 300 mm. This distribution of the deposition rate depends on the distribution

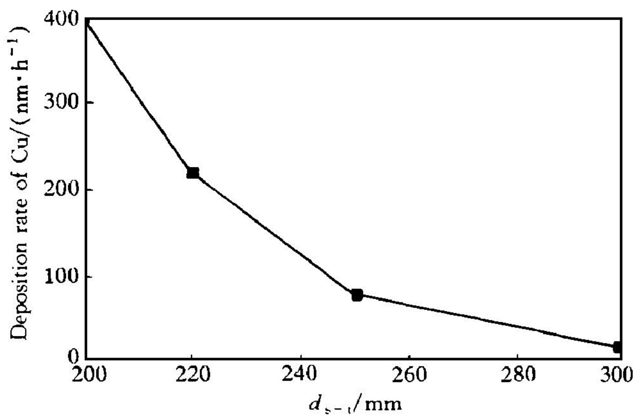

Fig. 3 Deposition rate of Cu on Si wafer with different d_{s-t}

of the magnetic field intensity in front of UBMS cathode. When d_{s-t} is larger than 100 mm, the axialmagnetic field intensity decreases rapidly. The transportation effect of the metal particles decreases obviously. The details are shown in Ref. [14].

3.3 Profiles of Cu in MePBII layer at different d_{s-t}

The profiles and the corresponding montage of Cu in MePBII layer at different d_{s-t} are shown in Fig. 4 and Fig. 5. It can be found that when d_{s-t} is 200 nm, the site of the concentration peak of Cu is on a distance of 33 nm from the surface and 12 nm to the position of the highest oxygen concentration, and the

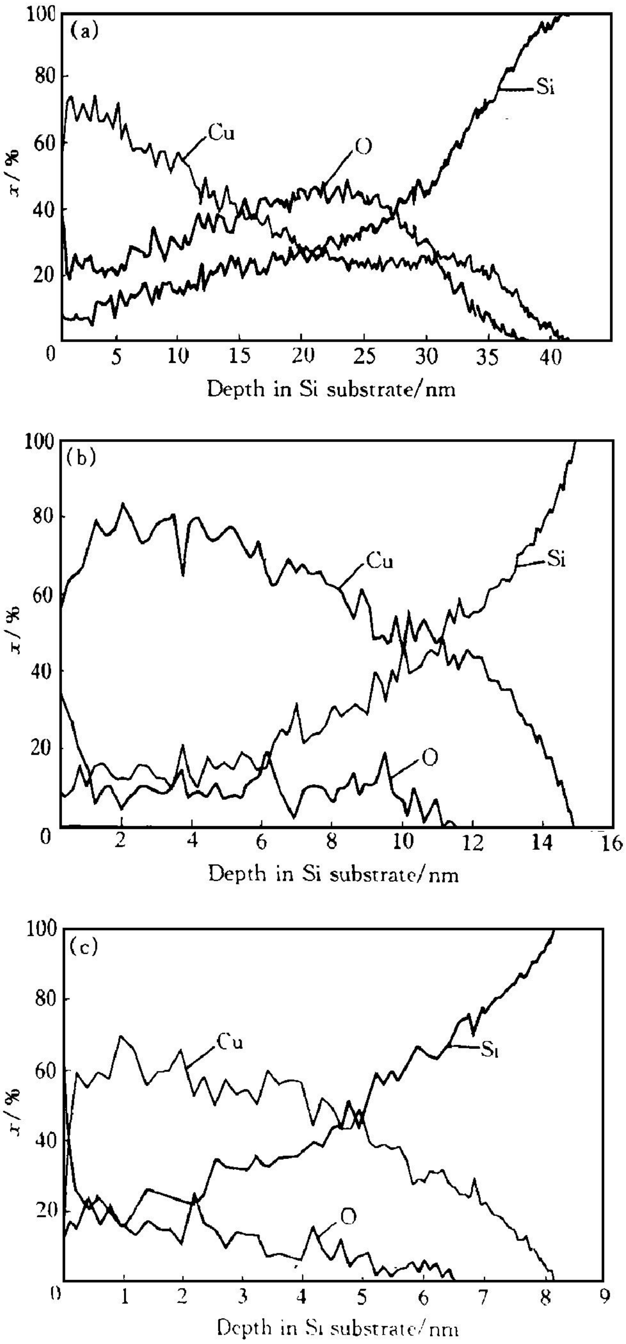

Fig. 4 Profiles of Cu implantation layer with different d_{s-t}
(a) —200 mm; (b) —250 mm; (c) —200 mm

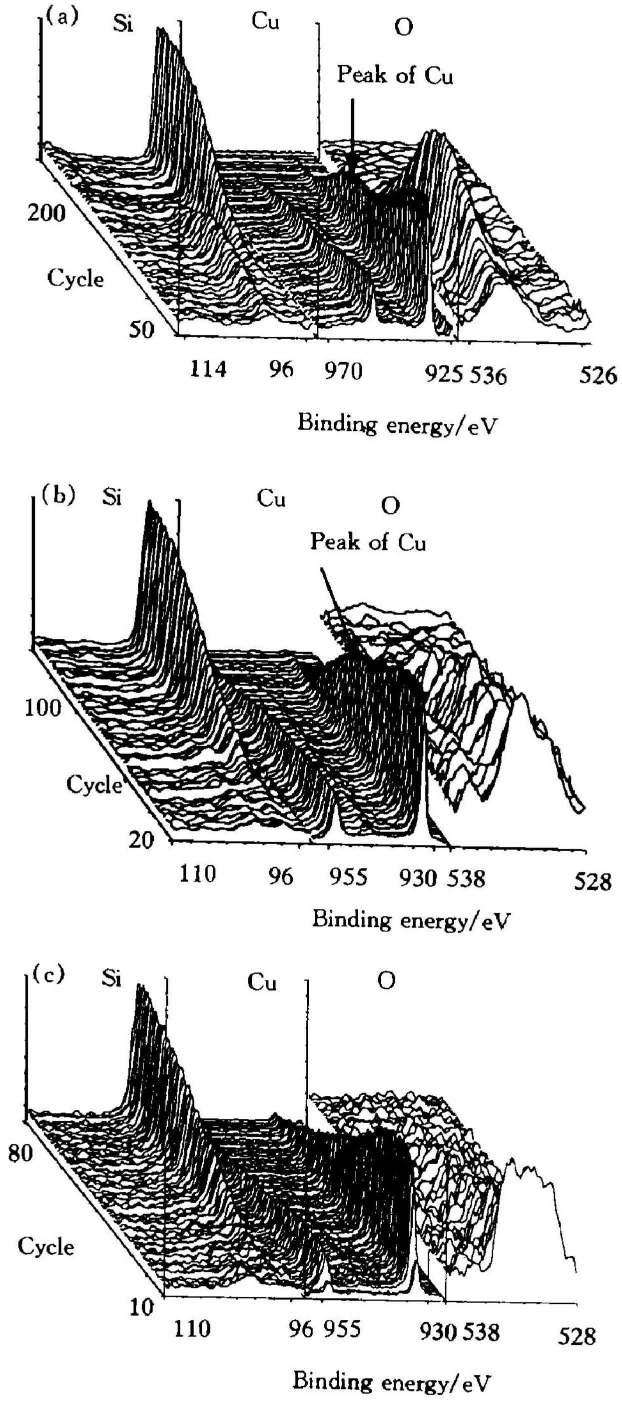

Fig. 5 Montges of Cu implantation layer with different d_{s-t}
(a) —200 mm; (b) —250 mm; (c) —200 mm

content of Cu peak is about 28% (mole fraction). It proves that the pure implantation of Cu ions happens at the initial stages of implantation process. According to the computation in previous section, the main process is the implantation by Cu ions of 20 keV. The type of the implantation changes gradually to the recoil implantation with increasing the deposition thickness. The depth of Cu atoms (25 nm) implanted in this process is much more large due to the multiple recoil implantation. This depth is approximately equal to the depth at which Ar ion is the maximum in Si substrate. So Cu is mixed with Si and O and the pure implantation of Cu becomes unimportant due to the obstruction of Cu film. Only pure implantation of Cu happens due to the reduction of deposition rate and increasing of ionization rate of Cu when d_{s-t} is 250 mm and 300 mm, respectively. Similar to the pure metal ion implantation, no obvious concentration peak of Cu appears in the profiles of Cu because of the strong sputtering effect of Cu ions, as shown in Fig. 4 (b) and Fig. 4(c). But a blurred concentration peak of Cu can be made out in the montage of Cu spectra when the d_{s-t} is 250 mm (Fig. 5(b)). It means the weak pure implantation still happens. The thickness of oxidation layers on Si surface decreases with increasing d_{s-t} owing to the sputtering of the implantation ions. In addition, the concentration of O in Si surface becomes low and spreads deeply in Si substrate due to the collision cascade of Ar^+, Cu^+ ions with O in original Si surface layer.

3.4 Profiles of Cu in MePBII layer at different pulse bias

The energy of Cu ions is decided by the pulse bias of MePBII. The profiles of Cu with different U_p when d_{s-t} is 200mm are shown in Fig. 6. It can be seen that the depth of the implantation layers decreases obviously and the type of the implantation changes from pure implantation to pure recoil implantation with decreasing U_p. The total amount of Cu atoms on Si substrate surface decreases gradually with the increase of the bias if the volume swell produced by Cu implantation is considered. This phenomenon is obvious when the bias changes from 60kV to 40kV. It is because of different sputtering effect. Thus, the factors resulting in deep implantation layer at high U_p(60kV) are not only the implantation with higher Cu ions but also the strong re-sputter effect. At the same time, the re-sputter effect can remove the weak-binding atoms to improve the surface quality of the sample. Of course, the too high bias can reduce the density and roughness of the implantation layer and influence the bind force of the film subsequent formed.

The microcosmic physical process of MePBII can be divided into four parts: 1) the metal particles (include ions, atoms and cluster of ions and atoms etc) deposition in the time intervals of the pulse (Fig. 7 (a)); 2) during the pulse, the pure implantation of gas ions and metal ions that come from the UBMS plasma and the particles re-sputtered from the film; 3) the recoil implantation of the atoms in the film; and 4) the re-sputter of the film (Fig. 7(b)). If the deposition rate is much larger than the rate of the recoil implantation and the re-sputter, The thickness of film on the substrate increases rapidly. The pure implantation only occurs at the initial stage of the process. Then the metal ions are mainly implanted into the metal film formed on the substrate. The thickness

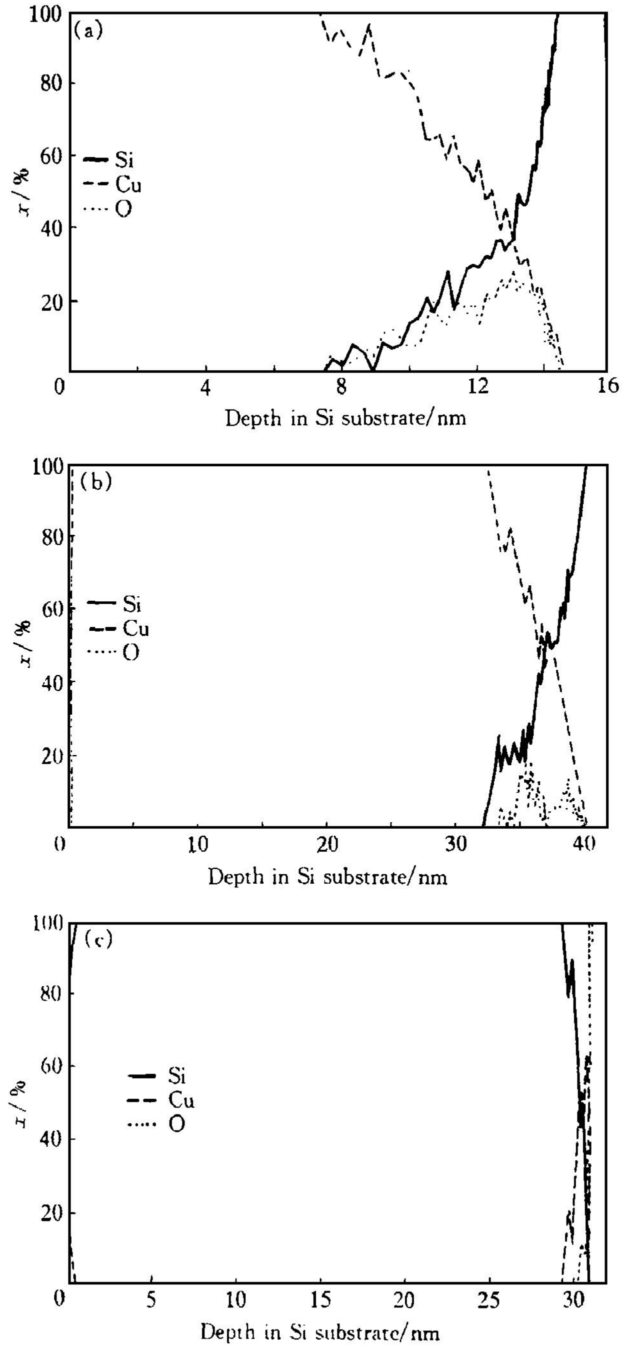

Fig. 6 XPS depth profiles of composition of implantation layer prepared with different pulse bias
(a) —40kV; (b) —20kV; (c) —0kV

of the deposition layer increases ulteriorly, the implantation effect becomes weaker and weaker. When the deposition rate is near those of the recoil implantation and the re-sputter rate, the recoil implantation, the deposition and/or the pure implantation happens at the same time. When deposition rate is lower than the re-sputter rate, only pure implantation of metal ions happens. Which process is prior to the others is decided by the selection of the parameters, such as U_p and d_{s-t}. If the substrate atoms is very easily sputtered (such as Ag, Cu, Au etc), the deposition rate of metal particles are too small and few implantation ions is found in the surface layer.

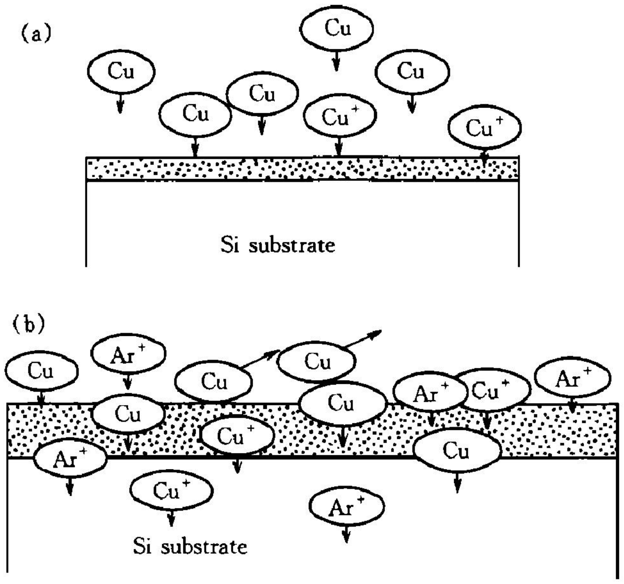

Fig. 7 Process of deposition, sputter and implantation of metal species in a pulsed period
(a) —Deposition process of metal particles in off-time of pulse; (b) —Implantation, redeposition and resputtering process in on-time of pulse

4 CONCLUSIONS

1) The metal ion implantation can be carried out using the UBMS plasma to generate metal plasma.

2) The deposition, the pure implantation, the re-sputter and the recoil implantation are decided by the parameters, d_{s-t} and U_p.

3) For the Cu implantation into Si substrate, if a lower pulse bias and the smaller d_{s-t} are selected, the deposition rate exceeds the recoil implantation and the re-sputter rate of the metal atoms and the thickness of the metal film on Si substrate increases rapidly. The implantation effect only occurs at the initial stage of the process, and changes to the process of the Cu implantation into the film of Cu, and results in a thick Cu film forming on the surface of Si substrate.

4) When high pulse bias (60 kV) and the small d_{s-t}, namely the deposition rate is near the recoil implantation and re-sputtering rate, both the recoil implantation and the pure implantation happen.

5) When high pulse bias (60 kV) and large d_{s-t} are selected, namely the deposition rate is lower than re-sputtering rate, only metal ion implantation occurs.

6) The influence of U_p on the type of the implantation is remarkable, the pure implantation sharply changes to the recoil implantation when U_p changes from 60 kV to 40 kV.

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