Ceramic Coating Technology

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This is one of the example of the application of ceramic coating, adopted for the first wall of the nuclear fusion testing devcice. The name of the testing device is JT-60. In early period, designers tried to adopt ceramic solid tiles. Although vacuum chamber will suffer distortion by high power magnetic field to a significant degree, they could not stand. After all, TiC coated MO tiles were adopted for this use.

If you decrease deposition temperature down to 500°C, you can not obtain enough adhesion strength of TiC onto the substrate, MO. And, if you increase deposition temperature over 950°C, you would deteriorate MO substrate. So, we de veloped the special plasma CVD. Deposition temperature is roughly 800°C - 900°C. The thickness of TiC is about 20 micrometer.

All these tiles are TiC plated. This is the picture of the tiles. Another example of ceramic coating is the TiN coated WC drills, as shown here. Another example is TiN coated high speed drills. Oil is injected through holes of the TiN coated WC drill. They are quite popular in Japan. SiC coated graphite is another example and it is used as the parts for the silicon epitaxy and impurity doping into silicone wafer.

Now let's move the subject to diamond film. Dr. Sedaka gave a lecture and he explained how the diamond film can be formed in vapor phase. Let's review the basic properties of diamond. Diamond of type I includes considerable amount of nitrogen. Type II includes for less amount of nitrogen. The electrical resistance of type I falls in the value of 10^4-$10^6 \Omega \cdot cm$. But II-b type is semiconductor, and includes the aluminium and boron as impurities. The thermal conductivity of I type is 2 times of that of copper and that of II-type is 4 times of that of copper.

Also, we produce those of crystals by high pressure technology. These are sliced down to small and thin plate and are used for the substrate of heat sink. If you dope Boron, the color will change to blue.

Now let's further look to the diamond polycrystalline film. So far, I talked about synthesis of diamond by high pressure technique. Now, as Dr. Setaka explained, small fine grain of polycrystalline film can be formed by cracking hydro-carbon gas mixed with diluted hydrogen. And one of the product for the application of this process is acoustic vibrating diaphram for speaker.

If you increase frequency mode up to 45 KHz. You can easily see some high degree of unharmonic distortion was caused on Titanium diaphram. The diamond plated ceramic does not show such distortion. However, diamond plated ceramic speaker diaphram can stand up to 50 Hz and distortion of diamond plated ceramic is much less than conventional Titanium diaphram. Now when you change the deposition condition of diamond, you can decrease the grain size of the crystal of diamond. These crystals are few tens anstrom in size. If we change the condition, such that deposition temperature is around 100°C or so, we have so called i-carbon i.e. diamond like transparent carbon film. In this case, you have two micron thick amorphous diamond or diamond-like transparent carbon film onto the substrate. In this case, substrate is silicon and interference color can be attained. This is one example how the interference color can be attained. This is just a example how the color of this amorphous diamond like.This is another example. If you change direction, the color changes, you know, from red to green, or purpple. This diamond-like carbon plated acoustic diaphram is used for tweater. The company SONY adapted this tweater. The sound is very clear, particularly at high frequency level.

Now let's talk about basic study which we are undergoing for diamond film. So far, we discussed on the application of crystalline diamond and amorphous diamond-like transparent carbon.

Now let's change the subject to single crystal diamond formation. Diamond can be a semiconductor as a silicon and galum-alsenide, silicon carbide as a band gap is high. So if you notice this value, it can be used for high temperature diode but the trouble comes from the fact that it is very expensive.

Both N type and P type have quite high carrier mobility, is much higher than that of silicon. Dielectric constant is about half of silicon that means it can be used for high frequency IC circuit package. Thermal conductivity is also very high. Natural diamond is purchased and we plated diamond onto it. This is single crystal. So, diamond epitaxy can be attained. This is undoped. If you dope boron during the diamond of epitaxy, the color changes to blue as you get it in high pressure technology case. Well, diamond film is very difficult to be analysed. However, this is one example how the film was analysed. We used low energy electron loss spectroscopy technique. Natural diamond and diamond film deposited on single crystal diamond were analysed. For graphite spectrum curve looks like this in the plasmon range of loss spectroscopy but natural diamond shows distinctively different curve. Diamond film resembles to that. If you dope boron, the shape of spectrum curve is somewhat distorted. Probably some strains were created. In P type doping case, phosphorus was doped in this case, and the color turned to reddish and the film is also slightly distorted.

We just checked doping profile and this is the profile examined by SIMS. We grew diamond film expitaxially and di-boron was mixed with a methan to 20,000 ppm. If you dope phosphorus during epitaxy, then, the curve showing doping level is rather more waving, shaking, like this, it means that phosphorus is very hard to be dopped. If you have decreased methan to hydrogen ratio you get more better crystallity.

This exhibits electronic properties but vertical axis is a resistivity and horizontal axis is a doping ratio, then if you dope boron during diamond growth then you lower the resistivity down to 10 Ω·cm or less, if you dope phosphorus during diamond growth you get down to 10-30 Ω·cm as low as boron case, but anyway it's fairly electricially conductive rather. We check a hall coefficient. Mobility is still as low as 620 in case of phosphorus doped N type semiconductor. Resistivity is down to 12 Ω·cm. Carrier concentration is another less than boron case.

Mobility is 1/3 of boron case. Checking the activation energy we get about 0.015 electron volt in case of boron doping.

SEDAKA discussed and explained that hydro-carbon radical is necessary to form a diamond crystal in vapor phase. And plasma is one of the method to create it.

another method creating the radical is conducted with the Ar-F Exima laser which has 193 nm in wavelength. The method is invented at the OSAKA University collaborated with our groups.

This illustration shows the optical micrograph 20 thousand magnification by SEM apparently shows the diamond crystal formation.

Electron diffraction and X-ray diffraction also turn out that the peak coincides to that of diamond. If you change the angle of Exima laser, the density of nucleation changes.

Conclusion

Ceramic coating and diamond coating are a young field. And so application is still very much limited.