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Feasibility using ethanol-added argon instead of helium as the carrier gas used in atmospheric-pressure plasma chemical vaporization machining

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Abstract
As a highly efficient noncontact chemical ultraprecise figuring technique, atmospheric-pressure plasma chemical vaporization machining (AP-PCVM) using helium as a carrier gas has been practically applied to improve the thickness uniformity of quartz crystal wafer. Because of the high cost and limited supply of helium, it is necessary to find a substitute for helium. As is well known, argon plasma at atmospheric pressure form arc streamers easily due to the high breakdown voltage. But it has been reported that the addition of a small amount of ethanol makes it possible to generate a stable glow discharge atmospheric-pressure argon plasma. In this report, feasibility of using ethanol-added argon instead of helium as the carrier gas used in AP-PCVM was investigated. A uniform, stable glow discharge CF_4 plasma was generated by applying the ethanol-containing process gas. Comparative experiment was conducted on quartz crystal wafer by AP-PCVM using helium and ethanol-added argon as carrier gas. As the result, using ethanol-added argon as the carrier gas in AP-PCVM instead of helium, the same etching rate was obtained and the operation cost was reduced.

Ethanol-added argon, atmospheric-pressure plasma chemical vaporization machining (AP-PCVM), quartz crystal wafer

1. Introduction

In the recent commercial production of quartz resonators, a wafer process has been intensively developed to improve the productivity of resonators. To improve the productivity of resonators by reducing the processing time for frequency adjustment, a uniform thickness is essential for the quartz crystal wafer. However, thin quartz crystal wafer broken easily using conventional mechanical fabrication process [1]. As a highly efficient and damage-free thickness correction technique, atmospheric-pressure plasma chemical vaporization machining (AP-PCVM) has been applied to improve the thickness uniformity of quartz crystal wafers [2].

AP-PCVM is an ultraprecise figuring technique that uses fluorine radicals generated by atmospheric-pressure plasma to change the surface atoms of a substrate into volatile reaction products to form the desired shape. Since AP-PCVM is a noncontact chemical figuring technique that does not apply a mechanical load to substrates, the breakage of thin brittle materials is prevented and no subsurface damage (SSD) layer is formed during the chemical removal process [3-4]. In our previous research, the thickness uniformity of a commercially available quartz crystal wafer was decreased from 250 to 50 nm by a single correction process without the formation of SSD [2]. KYOCERA has developed the world's smallest crystal unit (1.0 × 0.8 mm) for smartphones, wearables, and other electronic devices by applying AP-PCVM. However, helium gas has been used as the carrier gas in AP-PCVM until now. The helium gas used in industry is mostly produced from natural gas. Problems such as the depletion of natural resources and a high cost are of wide concern. To solve these problems, research on using argon gas instead of helium gas as the carrier gas, as it can be industrially produced by the fractional distillation of liquid air, in the generation of atmospheric-pressure plasma has been proposed. Although the operation cost can be reduced by using argon instead of helium, filamentary arc streamers formed easily in argon atmospheric-pressure plasma [5-6]. The addition of ethanol to argon has been proven to be very useful for generating an atmospheric-pressure glow discharge plasma, as reported by Sun *et al.* [7]. But in their work, there was no etching gas was added into argon. In our study, we used argon with a small amount of ethanol instead of helium as the carrier gas and CF_4 as the etching gas in AP-PCVM. Experiments were conducted to investigate the etching characteristics of quartz crystal wafers by AP-PCVM using ethanol-added argon-based atmospheric-pressure CF_4 plasma.

2. Experimental setup

Fig. 1(a) shows the experimental setup of AP-PCVM used in this study. Four flow paths exist, one for the carrier gas, one for the ethanol, and two for the process gases (CF_4 and O_2). The flow rates of the carrier gas and process gases were controlled using mass flow controllers (MFCs). Ethanol vapor was introduced using the gas-liquid mixture vaporization method. The carrier gas (Ar) and liquid ethanol (concentration 99.5%), where the latter was controlled using liquid mass flow controller (LMFC), were heated and mixed together in the vaporizer. The mixture gas was supplied from the center of the electrode and flowed through the space between the aluminum alloy electrode and the alumina ceramic cover arranged coaxially with the electrode.

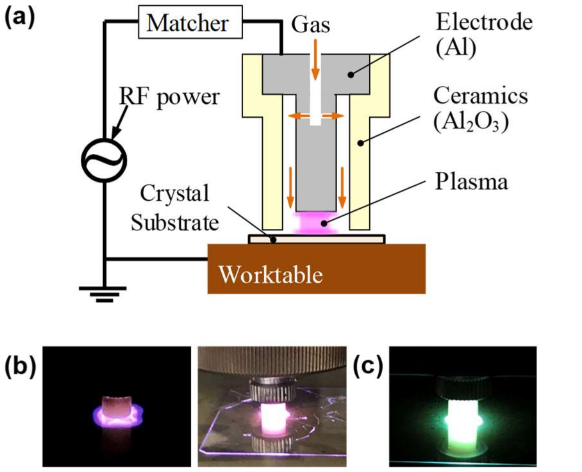

Figure 1. (a) Schematic of the experimental setup used for AP-PCVM. (b) Image of AP-PCVM on a quartz crystal wafer without adding ethanol. (c) Image of AP-PCVM on a quartz crystal wafer using ethanol-added argon.

The size of the AT-cut quartz crystal wafers used in the experiment was 54 mm × 50 mm × 90 µm. All the AP-PCVM experiments in this paper were conducted at room temperature (23.3 °C) without substrate heating. Fig. 1(b) shows a photograph of argon plasma generated on a quartz crystal wafer without adding ethanol. The high breakdown voltage of argon led to the formation of filamentary arc streamers, and the quartz crystal wafer was easily broken because of the high temperature due to the localized arc discharge. In addition, since the state of the localized arc discharge was unstable, the reproducibility of the removal spot formation was low. Fig. 1(c) shows a photograph of ethanol-added argon plasma generated on a quartz crystal wafer. By adding ethanol, a stable glow discharge plasma without filamentary arc streamers was formed and the quartz crystal wafer was not broken. And the reproducibility of the removal spot formation was improved. Thus, it is possible to precisely correct the thickness distribution of quartz crystal wafers by numerically controlled AP-PCVM using ethanol-added argon instead of helium as the carrier gas.

3. Results and discussion

In our previous research, helium gas was used as the carrier gas in AP-PCVM [2]. To investigate the difference between He and Ar-based CF_4 plasmas, a comparative experiment was conducted. The RF power was 60 W and the ethanol flow rate was 0.003 g/min. The carrier gas was He/Ar (600 sccm) and the process gases were CF_4 (10 sccm) and O_2 (4 sccm). The processing time was 15 — 90 s. Fig. 2 shows photographs and optical emission spectroscopy (OES) spectra of plasma generated on quartz crystal wafer using helium and ethanol-added argon as the carrier gas respectively. In the case of using helium as the carrier gas, the ionization potential for He is 24.6 eV, and two high-energy metastable states He (2^3S_1), 19.82 eV, He (2^1S_0), 20.6 eV can be formed in the discharge [8]. Because plasma was generated in atmospheric-pressure and the ionization energy of N_2 (15.58 eV) is lower than the potential energy of the two high-energy metastable states of He atoms. It is easy for He atoms in the high-energy metastable states to ionize N_2 molecules to generate N_2^+ ions at the He/air interface via Penning process. The OES spectra of the plasma using He as the carrier gas also confirmed this. Strong peaks corresponding to N_2 was observed. On the contrary, in the case of using Ar as the carrier gas, the ionization energy for Ar is 15.8 eV, and the metastable state Ar ($4^3P_2{}^0$), 11.6 eV, which is lower than the ionization energy of N_2. Penning process can not occured at the

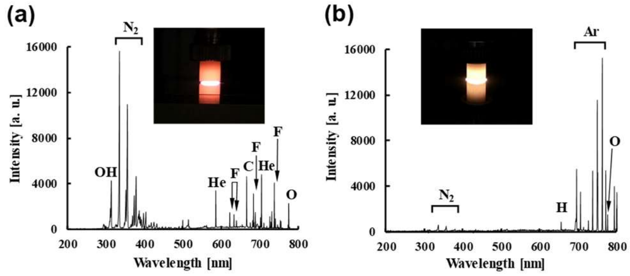

Figure 2. Photographs and OES spectra of plasma using helium (a) and ethanol-added argon (b) as carrier gas.

Ar/air interface, and filamentary arc streamers formed as shown in Fig. 1(b). When we add a small amount of ethanol into Ar, because the ionization energy for ethanol (10.47 eV) is lower than the potential energy of the high-energy metastable states Ar atoms [9]. Penning process occured and stable glow discharge plasma was generated as shown in Fig. 2(b). Furthermore, there was no strong N_2 peak was observed in OES spectra. In addition, as He has a much lower mass than N_2, and Ar has a higher mass than N_2. So the area of plasma using ethanol-added Ar as the carrier gas is wider than that of using He as the carrier gas. The diameter of the removal spot formed using ethanol-added argon as the carrier gas was larger than that of the spot formed using He, but the maximum depth was lower [10]. The removal rate using He and ethanol-added argon were almost the same.

4. Conclusions

In this study, a stable glow discharge CF_4 plasma was formed using ethanol-added argon as a carrier gas. Comparative experiment was conducted on quartz crystal wafer using helium and ethanol-added argon as the carrier gas. Although the shape of the removal spot was different using helium and ethanol-added argon, almost the same volumetric removal rate was obtained. Using argon instead of helium as the carrier gas in AP-PCVM will effectively solve problems such as the depletion of natural resources and high cost.

Acknowledgements

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