リモート型ホットワイヤ装置の開発と新規MEMSプロセスへの応用

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論文内容要約

Hot wire method has been used for CVD (chemical vapor deposition) of Si-based thin films, such as a-Si (amorphous Si) and p-Si (polycrystalline Si), as a useful surface reaction method for semiconductor process. Hot wire method is known as gas decomposition or activation method via catalytic reaction on heated metal catalyzer called “hot wire”. In this method, process temperature can be lower than thermal activation method, but reaction efficiency is higher than plasma activation method. It is because that, almost of important reaction is carried out by catalytic reaction on a hot wire, which is two-dimensional surface. Must be heated part is a hot wire, but not a substrate. In addition, plasma is reaction between electrons, ions and molecules, which is like point-to-point reaction. In contrast, hot wire is reaction between molecules and hot wire surfaces, which is like point-to-surface reaction. This is the reason why gas utilization efficiency in hot wire method is much higher than plasma method. On the other hand, hot wire method can also be used for a high density radical source. Generated atomic hydrogen density is 2–3 orders of magnitude higher than that in plasma. Thus, it is used for radical irradiation processes, such as cleaning of substrate surface, reduction of metal oxide, removal of photoresist and radical doping.

For these reasons, hot wire method is also quite attractive method for MEMS process, thus we started this research with the motivation for development of novel MEMS processes using hot wire process. Conventionally, open type hot wire tool where a hot wire and a substrate are located in the same chamber has been used. However, in this tool, a substrate is strongly heated by radiation from a hot wire. This is a big issue to apply MEMS process, because MEMS sometime has some micro structures, which are thermally isolated from the substrate. Because of that, we firstly developed new concept of hot wire tool, which can be applied for MEMS process. After that, atomic hydrogen enhanced CVD of ZnSe and atomic hydrogen pre-treatment method for Cu-Cu hermetic bonding were developed as MEMS process applications.

To decrease radiation from a hot wire, we figured out the concept of new type of hot wire tool, which has structurally separated 2 of chambers. The first one is the hot wire chamber, which has a hot wire in glass tubes. Radicals are generated by a hot wire, but most amount of radiation is emitted to outside of the chamber. The second one is the main chamber where a substrate is located in. A substrate is not strongly heated by radiation, because distance between the substrate and the hot wire is 100–300 mm. In addition, reactant gases such as oxidation gases and CVD source gases are introduced into the main chamber directly. Thus, introduced reactant gases do not react with the hot wire, directly. On the other hand, high density of radicals must be conveyed to the substrate at the same time. It is considered that radicals are deactivated by collision with chamber wall during remote transportation. Thus, radicals are conveyed by high velocity of viscous flow, which can decrease collision number with chamber wall. In addition, the hot wire chamber is consisted quartz tube, which deactivation rate of radicals is lower than metals.

As results, the substrate temperature was heated up 5–50°C, even though the hot wire was heated at 2000°C. This is drastically reduction, because the substrate was heated up 150–250°C in case of the open type setup. On the other hand, high density of atomic hydrogen could be conveyed to the substrate. It was estimated that 2.0×10^{10}–2.0×10^{13} cm^{-3} of atomic hydrogen was conveyed to the substrate by the measurement using WO_3 doped phosphate glass. Even when atomic hydrogen density was the highest value as 2.0×10^{13} cm^{-3}, the substrate was heated up only 10–50°C. This density is 2–3 orders of magnitude higher than that in plasma, and the same level or 1 order of magnitude higher than that in the open type hot wire tool.

As the first application of the remote type hot wire tool, ZnSe CVD was carried out. ZnSe is known as an IR material which has wide and flat transmittance window. In particular, ZnSe is the only material which can transmit finger print region in the range of 7.7–15.4 µm, which shows specific absorption in each substance. Thus, ZnSe is the only available material for IR window of substance identification application, such as gas sensor. Thus, it is considered that ZnSe IR window is quite attractive to develop MEMS IR sensors.

In this research, we proposed ZnSe CVD using hot wire process, which can achieve lower substrate temperature, but higher deposition rate than plasma. It was considered that high density of atomic hydrogen can decompose source gases efficiently. As a result, the highest ZnSe deposition rate was obtain at 300°C of the substrate temperature. ZnSe was not deposited below 100°C and above 400°C. However, ZnSe deposition rate using remotely irradiated atomic hydrogen was several nm/min, which is the same level of usual PECVD method. It is considered that a few orders of magnitude higher atomic hydrogen is not drastically improve gas decomposition efficiency.

On the other hand, ZnSe film was also deposited on the glass tube which is located around the hot wire, at 2.2 µm/min of sufficiently high deposition rate. In addition, only Zn and Se are identified from the ZnSe film by the XPS (X-ray photoelectron spectroscopy) measurement. It means that carbides and oxides derived from organic metals, and W compounds derived from W hot wire were not contaminated into ZnSe film. It is considered that carbides and oxides were removed by irradiated atomic hydrogen, and W hot wire was not damaged by direct reaction with source gases. In addition, transmittance range of IR was at least the wavelength of 5–15 µm, which can cover the finger print region.

Actually, high deposition rate ZnSe CVD was not achieved using remotely transported atomic hydrogen, but sufficient deposition rate was obtained by direct decomposition on the hot wire surface. Nearby the hot wire, radiation heating is the biggest problem for MEMS application, however, it is considered that the ZnSe film was not heated above 400°C. It is because that, ZnSe was not deposited at 400°C of substrate temperature in the prior CVD trial. Thus, even though direct source gas decomposition is required for high rate deposition, it can be considered that high rate deposition below 300°C is possible.

As the second application, a new pre-treatment method for wafer level Cu-Cu hermetic bonding using atomic hydrogen irradiation generated by hot wire is developed. The role of atomic hydrogen is not only Cu oxide reduction but also suppression of oxidation of Cu surface in atmospheric air. The treated Cu can be hermetically bonded exposing in air by conventional bonding system without any extra treatments. Thus, this technology allows hermetic sealing process using Cu instead of Au without losing fabrication process flexibility. It is attractive from material cost reduction and metal contamination points of view. Such air exposable hermetic Cu-Cu bonding technology has not been reported before, and it is the first time to investigate the mechanism why atomic hydrogen irradiated Cu is not oxidized.

Re-oxidation suppression effect was observed by the AES measurements. The citric acid treated Cu was easily re-oxidized in air, but the atomic hydrogen treated Cu was not easily re-oxidized even passed 1 day. On the other hand, thermally desorbed molecules were observed by the TDS measurements. Then, it was found that much amount of H_2 was desorbed from the Cu films which can suppress re-oxidation. In addition, magnitude of re-oxidation suppression effect was strongly related to H_2 desorbed amount. Therefore, it is considered that the mechanism of re-oxidation suppression effect of the atomic hydrogen treated Cu is derived from chemisorbed hydrogen atoms on the Cu surface. For these observations and re-crystallization temperature of Cu (150°C), standard atomic hydrogen pre-treatment condition was decided at 100°C for 10 min.

After that, Cu-Cu bonding was carried out using the optimized atomic hydrogen pre-treatment condition. As results, a pair of the citric acid treated substrates was hermetically bonded above 350°C. In contrast, the atomic hydrogen treated one could be bonded at 300°C even exposed air for 1 day. This acceptable interval time to bonding is sufficient to transport bonding wafers to a bonding tool from a hot wire tool. Thus, this atomic hydrogen pre-treatment process is practical for usual bonding process.

Gas pressure of hermetically sealed cavity was estimated by zero-balance method, then the pressure was 5–7 kPa. This value is mostly same level as the calculated value by the TDS results. On the other hand, the pressure was decreased with time. It is considered that sealed gas molecules were re-adsorbed on the pure Cu surface. For 2 months of exposure to air, the sealed pressure was not increased drastically, thus it is considered that the leak rate is sufficiently low.

To show superior of the atomic hydrogen treatment using hot wire, some other pre-treatment methods were also investigated. As a result, H_2/Ar plasma treatment was the only method which showed the same level tensile strength compared as the formic acid vapor treated one, even exposed air for 30 min. The formic acid vapor treatment is carried out in the bonding chamber, thus H_2/Ar plasma treatment is superior from air exposable point of view. It is considered that H_2/Ar plasma treatment can also suppress re-oxidation by chemisorbed hydrogen atoms. However, Cu oxide reduction by H_2/Ar plasma treatment is available above 150°C, because generated density of atomic hydrogen is lower than that in the hot wire. Therefore, the atomic hydrogen treatment is the most superior pre-treatment process for Cu-Cu bonding.

Finally, superiority of the remote type hot wire tool was shown through the various MEMS process applications. In particular, it was clarified that the hot wire process was quite effective as a high density of radical source. Radical is one of the most important species in the chamber, and widely utilized various MEMS processes. Thus, it is expected that the hot wire method can be applied further various MEMS processes which is driven by radical reaction.