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Preparation of high performance SiN_x films deposited by reactive sputtering and PECVD at low temperatures

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Abstract

Growing interest in a high performance insulating films deposited at low temperatures arises in various thin film applications. We have examined the characteristics of insulating SiN_x films deposited by sputtering and PECVD at low temperatures. High performance films are obtained by sputtering without substrate heating. A cause of poor characteristic of low density in the PECVD films deposited at 200°C can be clarified by comparing characteristics with those by sputtering.

1. Introduction

Interest in low-temperature deposited insulating thin films of high performance has much grown in the applications to 2.5D/3D-LSIs, solar cells, organic electroluminescence displays, and so on.[1-3] Since SiN_x thin films are traditional insulating films, the performance of films deposited at low temperatures (less than 200°C) is ordinarily unsatisfactory to applications. In a previous paper, we have successfully prepared SiN_x films of high performance, which tolerates the Cu diffusion up to 700°C, by reactive sputtering without substrate heating[4]. Thus, we clarify possible causes of the degradation of low-temperature-deposited SiN_x films by comparing the characteristics of films deposited by sputtering and PECVD. This may contribute to show a guide to the successful preparation of SiN_x films at low temperatures. We report examinations taking notice of the chemical state of hydrogen atoms incorporated in films.

2. Experimental Procedure

An HF-solution and distilled-water rinsed p-Si(100) wafer was used as a substrate. After the pre-treatment of Si target with Ar + H_2 gas mixture, the SiN_x deposition was executed by rf. reactive-sputtering with an Ar + N_2 (+ H_2) gas mixture without substrate heating. PECVD-deposited SiN_x films were obtained in an apparatus with 13.56 MHz rf. using a SiH_4 + NH_3 + N_2 gas mixture at 200, 300, and 400°C. The thickness of SiN_x films is in the range of 100-500 nm. The obtained films were characterized by STEM equipped with EDX, X-ray reflectivity (XRR), and spectroscopic ellipsometry.

3. Results and Discussion

There is a considerable amount of literature concerning the characteristics of SiN_x films. Among them, a few are reported by sputtering. However, sputtering has been attracted much attention as a process to obtain SiN_x films intrinsically without substrate heating. Figure 1 shows the cross-sectional STEM images of the sputter-deposited SiN_x films.[5] Reactive sputtering of the Si target ordinarily brings about the formation of a layer consisting of Si and O on Si prior to the deposition of SiN_x [Fig. 1(a)]. This may result in a traditional conclusion that the sputtered SiN_x film has unsatisfactory properties. We can completely eliminate this layer by pre-treatment of the Si-target with an Ar + H_2 gas mixture, as seen in Fig. 1(b). We hereafter executed the ‘pre-treatment’ before the SiN_x deposition.

In Fig. 2, we show the relation between the nitrogen content in SiN_x films and the film density, where the film density increases toward the Si_3N_4 bulk value (3.44 g/cm^3) [6] with increasing the nitrogen content for sputtered films without substrate heating. On the other hand, the film density remains on the almost same level of 2.15~2.2g/cm^3, which is lower than that of SiO_2 (2.65g/cm^3)[7], regardless of the nitrogen content in the SiN_x films by PECVD deposited at 200°C. The dense films are known to be effective for suppressing the Cu diffusion in Through Si via (TSV) applications.[8] In this sense, the sputtered films show good characteristics.

Figure 3 shows the relation between the refractive index and the nitrogen content in the SiN_x films, where the refractive index is a good measure for the comparison of our data with others. Interestingly, the dependence is contradictory in films by sputtering and PECVD. For the PECVD films, the refractive index decreases with increasing the nitrogen content in films. The oxygen content in the films is also known to decrease the refractive index; however, the oxygen content in the present films is lower than 6 at.%, suggesting another cause. Figure 4 shows the interrelation between film density and refractive index for each SiN_x film, in which the refractive index of the PECVD-SiN_x films varies almost in the same range as sputtered films. Apparently, the sputtering is superior to PECVD in obtaining dense films at low temperature.

We take notice of the hydrogen content and chemical bonding state of hydrogen atoms incorporated in the

PECVD SiN_x films to clarify the cause of low-density films. In Fig. 5, the hydrogen content is plotted against the deposition temperature, which is derived from the results of FT-IR measurement. It is worthy of mention that the amount of hydrogen in the present films is reduced by one figure as compared that in the previously reported films ($10^{22}cm^{-3}$)[9]. From Fig. 5, the amount of incorporated hydrogen tends to increase with decreasing the deposition temperature. Especially, the amount of Si-H bonding increases with an increase of total amount of hydrogen. On the contrary, the amount of N-H bonding is insensitive to the increase in the total amount of hydrogen. This result indicates that the low density film arise from the Si-H bonding incorporated into the SiN_x films deposited at a low temperature. Claassen *et.al.* have reported that hydrogen atoms are incorporated into PECVD SiN_x films with a high Si/N ratio mainly as a Si-H bonding, while films with a Si/N ratio less than 0.75 include mainly as a N-H bonding.[10] Our films, a Si/N ratio is 0.83-1.0, well agree with their results, although the amount of hydrogen (6 at.%) is less than that of their films (23.7 at.%).

In this study, we clarify that the amount of hydrogen (also Si-H bonding) varies linearly with the deposition temperature, from which the amount of Si-H bonding mainly affects the characteristics of films. In the sputtered SiN_x films, on the other hand, a very little amount of incorporated hydrogen atoms is detected in the film by the H_2 addition in the sputtering gas, and the N-H bonding is dominantly increases as compared with Si-H bonding. In addition, a relatively dense SiN_x film can be obtained by Cat-CVD, in which the N-H bonding is mainly incorporated. Thus, we can conclude that a cause of the low-density PECVD SiN_x film is due to incorporation of the Si-H bonding during deposition at low temperatures.

4. Conclusions

We have examined the characteristics of low temperature deposited SiN_x films by sputtering and PECVD. It is revealed that the dense SiN_x films are obtained by sputtering without substrate heating, while films of low density are obtained by PECVD deposited at 200°C. Refractive indices, show different tendency owing to the deposition method; however, vary in the almost same range of value. The main cause of the PECVD SiN_x films of low density deposited at low temperature is the existence of Si-H bonding in the films, which is reciprocally proportional to the deposition temperature. Therefore, the present results suggest that relatively dense PECVD SiN_x films is possible to prepare if we can invent a method to decrease Si-H bonding in the film.

Acknowledgements

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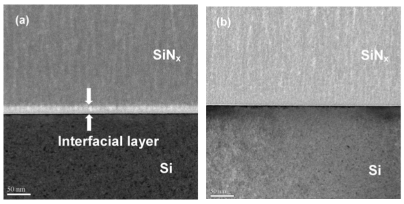

Fig. 1 Cross-sectional STEM images of SiN_x films on Si deposited by reactive sputtering: (a) without 'pretreatment', and (b) with 'pretreatment' with Ar + H_2 gas mixture.[5]

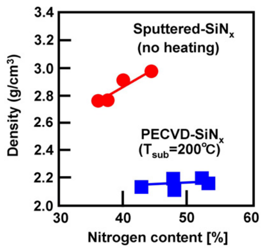

Fig. 2 Relation between nitrogen content in SiN_x films and film density.

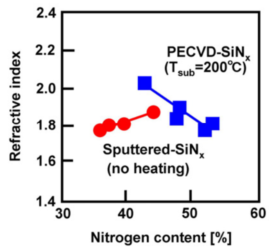

Fig. 3 Relation between refractive index and nitrogen content in SiN_x films deposited by sputtering and PECVD.

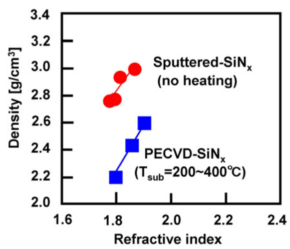

Fig. 4 Interrelation between film density and refractive index for each SiN_x film obtained by sputtering and PECVD with additional data deposited at increased temperatures.

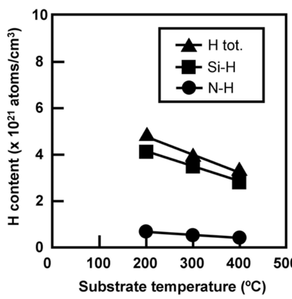

Fig. 5 Variation of hydrogen content and hydrogen bond configuration as a function of substrate temperature by PECVD.