

Hu S M. Properties of amorphous silicon nitride films.

J. Electrochem. Soc. 113:693-8, 1966.

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The properties of amorphous silicon nitride films, formed on silicon substrates both by reactive sputtering and by chemical vapor deposition, have been investigated for potential use as a new, multipurpose material to supplement or supplant silicon dioxide (SiO_2) for such applications as surface passivation, electrical isolation, and impurity diffusion masking. [The SC[®] indicates that this paper has been cited in over 95 publications since 1966.]

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"In the early 1960s, the formative years of planar bipolar devices and insulated-gate field effect transistors, the development of these devices was up against failure and reliability problems of a surface origin. Silicon dioxide (SiO_2), thermally grown on silicon substrates as surface films, was the material used for surface passivation in addition to its uses for electrical isolation and diffusion masking, but its limitations, especially as a barrier against pervasive sodium, became increasingly evident.

"In 1964, I joined a group involved in the study of the physics and the passivation of silicon surfaces. One of the projects was to search for new materials as improved substitutes or supplements for SiO_2 . Silicon nitride appeared to be a very attractive candidate, judged from the few physical properties then known of its crystalline form, but it would have to be in an amorphous form to be useful for our intended applications.

"In late 1964, I started work on the preparation of silicon nitride films by reactive sputtering. Since few properties of crystalline silicon nitrides, and none of the amorphous form, were known, I also had to simultaneously investigate many properties such

as etch rate, dielectric constant, refractive index, bandgap, and infrared absorption spectrum, which were needed for identification. Initially, I obtained films that were predominantly SiO_2 and electrically very leaky. Many efforts were then spent to remove trace oxygen and water from nitrogen, until predominantly silicon nitride films were obtained. I switched from DC to RF sputtering, then a rather new technology. I experimented with various sputtering parameters and sputtering system designs, while making correlations with the properties of silicon nitride films I had obtained. Meanwhile, a colleague, V.Y. Doo, was experimenting on the preparation of silicon nitride films by chemical vapor deposition. While I had been coordinating and doing most of the characterization of both types of silicon nitride films, another colleague, D.R. Kerr, contributed significantly to the electrical characterization. By mid-1965, we had established to our satisfaction that silicon nitride was almost everything we hoped it to be: it was extremely impervious to sodium, gallium, steam, oxygen, and phosphorus, and was excellent for surface passivation. The results were well received at the Electrochemical Society meeting in Buffalo, New York, October 11-13, 1965. A year later in Philadelphia, a special symposium on silicon nitride was held in which 18 papers were presented. Soon we discovered the phenomenon of charge injection and trapping in silicon nitride,¹ a discovery that later led to the development of MNOS nonvolatile memory devices. The subject paper is a detailed version of my Buffalo presentation.

"I believe that the reason the paper is so highly cited is that it is the first paper, and a very comprehensive one, on what was considered an extremely promising material. It is now an essential material in silicon microelectronics. It is used as an element of device structures for gate dielectric, for passivation, or for charge storage as in MNOS devices. It is also used in device processings such as in self-alignment, local oxidation, or surface planarization. A recent bibliography on silicon nitride² contains 601 references."

1. Hu S M, Kerr D R & Gregor L V. Evidence of hole injection and trapping in silicon nitride films prepared by reactive sputtering. *Appl. Phys. Lett.* 10:97-9, 1967. (Cited 75 times.)

2. Morosanu C E. A bibliography on silicon-nitride films. *Microelectron. Rel.* 20:357-70, 1980.