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THE PREPARATION OF THIN LAYERS OF Ge AND Si BY CHEMICAL HYDROGEN PLASMA TRANSPORT

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Abstract—It has been proved that the transport of Ge and Si in hydrogen plasma takes place under certain conditions. The transport is probably carried on by volatile hydrides of Ge and Si which are formed during the interaction of hydrogen plasma and the respective semiconductor. The semiconductor layers prepared by this method are compact and well adhesive to the substrate. When deposited on glass they had a polycrystalline structure.

Résumé—On a démontré, que dans le plasma d'hydrogène pourrait avoir lieu une réaction de transport de Ge et Si. Cette réaction est effectuée probablement au moyen des hydrides volatiles formés par une interaction entre le plasma d'hydrogène et le semiconducteur respectif. Les couches des semiconducteurs ainsi préparées sont compactes et adhésives à la base. Si c'est le verre qui est utilisé, c'est la structure polycrystalline de la couche qui en resulte.

Zusammenfassung—Es wurde gezeigt, dass in einem Wasserstoffplasma eine Transportreaktion von Ge und Si stattfinden kann. Diese Transportreaktion wird bewerksetlligt durch flüchtige Hydride, die durch eine Reaktion des Wasserstoffplasma und der diesbezüglichen Halbleiter entstehen. Die Halbleiterschichten, welche durch diese Reaktion hergestellt wurden, sind kompakt und haften gut an der Unterlage. Auf Trägern aus Glas haben diese Schichten eine polykristalline Struktur.

IN ABOUT the year 1920 a phenomenon was described by several workers, which was later called 'Chemical cathode sputtering'. This phenomenon was studied more closely by GÜNTERSCHULZE[1] in 1926. He showed that in a glow discharge in hydrogen an extremely strong cathode sputtering of some elements takes place which, however, differs from normal cathode sputtering in other gases. In his work Günterschulze described an experiment in which As, Sb, and Bi were sputtered, although they were not connected with the cathode, when they were placed separately in a positive glow discharge column. According to Günterschulze's idea the anomalous sputtering of some materials involves the formation of volatile and unstable hydrides. In the above mentioned paper Günterschulze describes the phenomenon as it appears with As, Sb, Bi, C, Se and Te. The hydrogen plasma transport of As, Se, and Te was also described by ING and CHIANG[2] in 1966.

It is well known[3] that a large number of elements form hydrides which are in many cases volatile and unstable. Therefore, it is probable that many other elements under proper conditions may be transported in a hydrogen plasma.

In this work we have performed a transport of Si and Ge by hydrogen plasma. Our experimental arrangement is shown in Fig. 1. A silica glass tube was used in all our experiments (for Ge transport molybdenum glass was used as well). A high frequency discharge (frequency of about 28 MHz, output of about 10 W) was initiated by means of an external electrode. Hydrogen diffused through a hot palladium tube was used. The hydrogen pressure was approximately 10^{-1} torr. The temperature of the tube wall outside the furnace was below 100°C. Layers of semiconductors were deposited on the substrate and on the tube walls when the temperature in the furnace reached 350°–400°C or 600°C for Ge and Si respectively. Under these conditions the rate of growth of the layers is in the

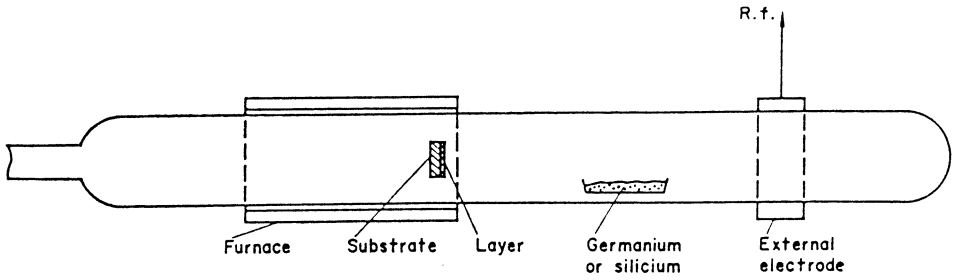

FIG. 1

order of 10^2A^0 per hr. When spectrally pure neon (WEB Technische Gase-Worke Berlin) instead of hydrogen under the same conditions was used, the transport did not take place.

The layers were compact and adhered well to the substrate (e.g. molybdenum or silica glass, Al, Ag). The X-ray analysis of the Ge layer deposited on glass proved this layer to be polycrystalline. The Si layer could be dissolved only in a mixture of HNO_3 and HF, indicating a crystalline structure.[4]

As to the mechanism of the transport we are able to present only a hypothesis to date. The transport is probably brought about by some volatile hydrides of Ge and Si which are formed during the interaction of the hydrogen plasma with the respective semiconductor. The transport takes place from the colder zone where the hydrides are formed to the hotter one where they are decomposed. The most stable hydrides GeH_4 and SiH_4 are gases and decompose rapidly at temperatures of about 350° and 600°C respectively.[3,5] It is interesting that these temperatures are equal to the temperatures of the substrate in our experiments.

The advantage of this method of preparing semiconductor layers is in their production at a relatively low temperature in a pure environment directly from Ge or Si. The transport rate is small, but we hope it can be increased by changing the temperature and the parameters of the discharge. Furthermore it is important that the reaction of hydrides decomposition under these conditions can be reversible. In this way even on an amorphous substrate polycrystalline layers may be produced and we hope to be able to prepare an epitaxial layer on a suitable crystal substrate.

The purpose of our work was to verify a possibility of Si and Ge hydrogen plasma transport. Our future work will be directed to a detailed study of transport conditions of the layers' growth and of their physical properties.

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