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GaN layers on Silicon with ZnO intermediate layer were synthesized by using the HVPE (Hydride Vapor Phase Epitaxy) method. ZnO layers were deposited from solutions of zinc compounds in ethanol or water in two steps. At the first step a ZnO nucleation layer was deposited from a solution of zinc acetate in ethanol, at the second step a ZnO precipitate was deposited from a solution of zinc nitrate and KOH in water by boiling. On the obtained structures the GaN nucleation layers were deposited at 500 °C for 15 min, then GaN layers were grown at 850–970 °C for 30 ± 5 min. Structures were studied by using the optical and SEM microscope and XRD method. The type of conductivity of the layers was determined by using the method of thermal electromotive force measurement (TEFM). The possibility of the electrical conductivity (EC) type changing from n- to p-type for the GaN layers deposited on silicon substrates with the use of intermediate ZnO layer deposited from solutions is demonstrated for the first time.